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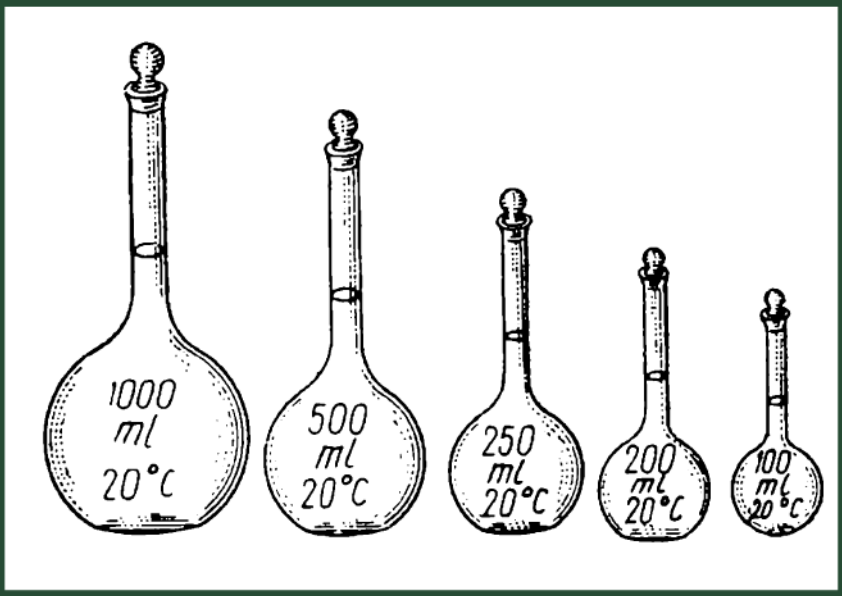
Ya. Gurevich

Analytical Chemistry



Mir Publishers Moscow

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АНАЛИТИЧЕСКАЯ ХИМИЯ

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА» ● МОСКВА

S. SHAPIRO,
Ya. GURVICH

ANALYTICAL CHEMISTRY

Translated from the Russian
by
D. SOBOLEV and Y. NADLER

MIR PUBLISHERS
MOSCOW

Revised from the 1968 Russian edition
First published 1972
Second printing 1975

This textbook gives the theoretical fundamentals of analytical chemistry and describes the laboratory practice of qualitative and quantitative analysis.

Special sections are devoted to the analysis of organic substances and to physicochemical analysis.

The chapters on qualitative and quantitative inorganic analysis have been written by S. Shapiro, Cand. Sc. (Chem.), and the sections "Analysis of Organic Substances" and "Physicochemical Methods of Analysis", by Ya. Gurvich, Cand. Sc. (Tech.).

The textbook is meant for students of vocational schools and can be used for training workers in industrial laboratories.

This book has been recommended for republication by Indian specialists under the programme of the Joint Indo–Soviet Board to make the best Soviet textbooks available for Indian students.

На английском языке

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Preface

Analytical chemistry studies the chemical composition of substances. Analysis may be qualitative or quantitative. Qualitative analysis is concerned with the detection of the presence or absence of elements in compounds and of chemical compounds in mixtures; quantitative analysis, with the determination of the relative proportions of elements in compounds and of chemical compounds in mixtures.

Chemical analysis is one of the most important methods of controlling raw materials, intermediates, and finished products, as well as the composition of air in shops and laboratories of industrial plants. In agriculture, chemical analysis is used to determine the composition of soils and fertilizers; in medicine, to determine the composition of medicinal preparations. There is hardly a branch of the national economy that can do without chemical analysis. Industrial progress as a whole and the production of new kinds of materials are closely associated with analytical chemistry. No production unit can put out high-quality products without thorough analytical control at all the stages of the technological process.

The course in analytical chemistry extends the knowledge acquired by the students in studying general, inorganic, and organic chemistry.

Information on qualitative analysis is expounded in the following order: first the characteristic reactions for all the ions of a given analytical group are described, and then each ion is characterized separately. Simultaneously, the chemical properties of compounds containing the ion in question are indicated in connection with the position of the corresponding element in the periodic table.

The laboratory portion of the book describes qualitative analysis by the semimicro method which, besides retai-

ning all the merits of the classical macro method, possesses a number of advantages over the latter: it takes much less time and reagents. Besides, working by the semimicro method develops carefulness and accuracy in carrying out analytical operations, which is a valuable asset in quantitative analysis.

The sequence of operations of ion separation is vividly illustrated in the textbook, making it easier to master analytical procedure. Control questions, exercises, and problems with answers are given in the corresponding sections and paragraphs to illustrate the principles presented in the text.

As lack of grounding in physical chemistry makes it difficult for students to master the section "Physicochemical Methods of Analysis", each method of analysis described is preceded by a brief account of the corresponding theoretical section of physical chemistry.

PART ONE

QUALITATIVE INORGANIC ANALYSIS

CATIONS

CHAPTER I

Concentration of Solutions and Ways of Expressing It

1. Solutions and Solubility

All substances are more or less soluble in water and each substance can be characterized by its specific solubility. The solubility of a substance is the maximum amount of the substance that can be dissolved in a definite quantity of solvent at a given temperature.

The solution is said to be *saturated* if the amount of dissolved substance in it is equal to the solubility of the substance at a given temperature. The solution is *unsaturated* if it contains an amount of dissolved substance that is less than its solubility, and is *supersaturated* if it contains an amount greater than its solubility at a given temperature.

In an unsaturated solution of a given substance it is still possible to dissolve an additional amount of the substance. Dissolving will continue until the solution becomes saturated. In a saturated solution it is impossible to increase the amount of dissolved substance (solute) without changing the temperature, volume, or pressure. Therefore, on introducing into a saturated solution an additional amount of the substance in the solid state, it will not be dissolved and will be present as a sediment in the solution.

A solution remains supersaturated until a precipitate is formed. If a crystal of the dissolved substance is added to a supersaturated solution, new crystals will immediately form around the one introduced; precipitation of crystals will continue until the solution becomes saturated. Crystallization can also be induced by shaking the solution or rub-

bing a glass rod against the inner wall of the vessel containing the solution. Thus, if the vessel contains both dissolved substance and a solid, the solution can only be saturated. If the solution were unsaturated the solid substance would dissolve, while a supersaturated solution is unstable and sooner or later a precipitate will appear in it and the solution will become a saturated one.

The solubility of a substance is usually expressed as grams of solute in 100 g of water or as moles (gram-molecules)[1] per litre of solution.

Examples: (a) the solubility of KCl at 20°C is equal to 34.0 g. This means that the maximum quantity of KCl that can be dissolved in 100 g of water at 20°C is 34 g, i. e., 134 g of a saturated solution contains 34 g of KCl and 100 g of water; (b) the solubility of $Na_2SO_4 \cdot 10H_2O$ is equal to 0.5 mole at 20°C. This means that 1 litre of saturated solution contains 0.5 mole (161.1 g) of $Na_2SO_4 \cdot 10H_2O$.

Solutions are also characterized as *dilute solutions*, in which the amount of solute is small as compared to the amount of solvent and the solution is far from being saturated; or as *concentrated solutions* with a high content of the solute.

Questions and Problems

1. Define the *solubility* of a substance.
2. What units are used to express the solubility of a substance?
3. Define the term *molar solubility*.
4. At room temperature 2.0 g of $CaSO_4 \cdot 2H_2O$ can be dissolved in 1 litre of water. Express the solubility of this salt in moles per litre.
Ans. 0.013 mole per litre
5. The solubility of $PbCl_2$ is 0.0356 mole per litre at 20°C. How many grams of $PbCl_2$ are dissolved in 1 litre of water at 20°C?
Ans. 9.90 g

2. Concentration Units

The concentration of a solution is the weight of a substance contained in a definite weight of solution or solvent (concentration by weight) or in a definite volume of solution (concentration by volume).

[1] A gram-molecule, or mole, is the quantity of a substance whose mass in grams is equal to its molecular weight.

The unit of volume used in analytical chemistry is a litre (lit) or one thousandth of a litre, a millilitre (ml); the unit of mass is a gram (g) or milligram (1 mg = 0.001 g). Besides, use is made of special chemical units of mass: gram-molecule (mole) and gram-equivalent[1] (g-equiv) — see Sec. 141.

The amount of solute in a definite quantity of solvent or solution can be expressed in various units: grams, per cent, gram-molecules or moles (molarity), gram-equivalents (normality) — see Sec. 142.

The concentration of a solution expressed in per cent is the number of mass units of solute contained in 100 mass units of solution. For instance, if the concentration of KCl is equal to 10 per cent, 100 mass units (say, 100 g) of this solution contain 10 mass units (10 g) of potassium chloride and 90 mass units (90 g) of water.

The concentration of a solution expressed as the number of moles of solute in 1 litre of solution is called the *molarity* of the solution and is denoted as M; solutions may be: molar ($1M$), dimolar ($2M$), semimolar ($0.5M$), decimolar ($0.1M$), centimolar ($0.01M$), etc.

The concentration of a solution expressed as the number of gram-equivalents of solute in 1 litre of solution (g-equiv/lit) is called *normality* and is denoted as N.

Gram-equivalent is denoted as E. Thus, for example, $E_{H_2SO_4} = \frac{M_{H_2SO_4}}{2} = \frac{98.08}{2} = 49.04$ g; i. e., a gram-equivalent of sulphuric acid is equal to half the gram-molecule.

Solutions may be: normal ($1N$), dinormal ($2N$), seminormal ($0.5N$), decinormal ($0.1N$), centinormal ($0.01N$), etc.

Hence, the normality of a solution indicates the number of gram-equivalents of solute contained in 1 litre of solution.

The concentration of a solution is sometimes expressed by its density since the latter at a given temperature corresponds to a definite content of solute in the solution. For example, a sulphuric acid solution with a density equal to 1.800 g/cm³ at 20°C contains 87.69 per cent H_2SO_4.

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[1] A gram-equivalent is the number of grams of a substance that is equivalent to one gram (1.008 grams to be more exact) of hydrogen in a given reaction.

To determine the concentration of a solution from its density use is made of reference tables (Appendix 4). Knowing the density of a solution, the content of solute in it in per cent is found in the reference table and the molarity and normality of the given solution is then calculated.

Example. Calculate the molarity and normality of a sulphuric acid solution with a density of 1.303 g/cm^2 at 20°C.

Solution. From the reference table we find that the H_2SO_4 solution contains 40.0 per cent H_2SO_4. Then we calculate the molarity and normality of the solution as follows. One litre of this solution weighs $1.303 \times 1{,}000 = 1{,}303$ g. To find the number of grams of H_2SO_4 contained in 1 litre of solution we must write the following proportion:

100 g of solution contain 40.0 g of H_2SO_4
1,303 g of solution contain x g of H_2SO_4

$$x = \frac{40.0 \times 1{,}303}{100} = 521.20 \text{ g/lit}$$

This means that 1 litre of the solution contains 521.20 g of H_2SO_4.

A molar solution contains 98.08 g/lit of H_2SO_4.

To determine the molarity of the solution we must write the following proportion:

98.08 g/lit — 1M
521.20 g/lit — $x M$

$$x = \frac{521.20}{98.08} = 5.31M$$

A gram-equivalent of H_2SO_4 is equal to $\frac{98.08}{2} = 49.04$ g.

To calculate the normality of the solution we must write the following proportion:

49.04 g/lit — 1N
521.20 g/lit — xN

$$x = \frac{521.20}{49.04} = 10.62N$$

Hence, a sulphuric acid solution with a density of 1.303 g/cm^3 has a concentration equal to 40.0 per cent and is a 5.31M and 10.62N solution.

Questions and Problems

1. Define the *concentration* of a solution.
2. What units are used to express the concentration of a solution?
3. What is the concentration of a solution expressed in per cent?
4. What are the *molarity* and the *normality* of a solution?
5. What weight of salt must be dissolved in 100 g of water to obtain a 10 per cent solution?

Ans. 11.11 g

6. 200 ml of a solution of sulphuric acid contain 4.90 g of H_2SO_4. Determine the molarity and normality[1] of the solution.

Ans. 0.25*M*; 0.5*N*

7. 300 ml of solution contain 0.3723 g of $Na_2S_2O_3 \cdot 5H_2O$. Determine the molarity of the solution.

Ans. 0.005*M*

8. Calculate (a) the concentration in grams per litre of a 14.0 per cent solution of KOH; (b) the molarity; (c) the normality of the solution if its specific gravity is equal to 1.118.

Ans. (a) 156.52 g/lit; (b) 2.78*M*; (c) 2.78*N*

9. Express the concentration of a 3*M* H_2SO_4 solution: (a) in grams per litre; (b) moles per litre; (c) gram-equivalents per litre.

Ans. (a) 294.24 g/lit; (b) 3 mole/lit; (c) 6 g-eq/lit.

10. Calculate the molarity and normality of solutions with a specific gravity of 1.066 at 20°C for: (a) H_2SO_4; (b) HNO_3.

Ans. (a) 1.09*M*; 2.18*N*; (b) 2.03*M*; 2.03*N*

CHAPTER II

Law of Mass Action. Chemical Equilibrium

3. Statement of the Law

When two substances react (taken, for instance, in the form of solutions) to form a new substance, the chemical reaction is manifested in a gradual decrease of the mass of the original substances (reactants) and a simultaneous increase in the mass of the resulting substances (reaction products). Some reactions proceed during an infinitely short period; they may be considered to be momentary reactions (for example, neutralization). Other reactions proceed so slowly that it is possible to determine the quantities of reacting and resulting substances at different stages of the process. Thus,

[1] To calculate the molarity and normality of a solution first determine the number of grams of solute per litre of solution and then divide this number by the appropriate gram-molecule or gram-equivalent.

when studying the rate of decomposition of hydrogen peroxide it is possible to determine the quantity of hydrogen peroxide decomposed or the quantity of oxygen evolved in a given period of time.

The rate of a chemical reaction is determined by the change in concentration of the reactants in a unit of time.

Chemical reactions occur only when particles of the reactants collide. The shorter the time interval between such collisions, the greater the quantity of substances that react in the same period of time. It is obvious that in more concentrated solutions the number of collisions is greater. Consequently, the rate of reaction depends on the concentration of the reacting substances. This dependence that has come to be known as the *law of mass action* can be stated as follows: *the rate of chemical reaction is directly proportional to the product of the molar concentrations (mole/lit) of the reactants.*

If we denote the rate of a given reaction as u, the concentration of the reactants as C_1 and C_2, and the proportionality coefficient as K, then according to the law of mass action

$$u = KC_1 \cdot C_2 \qquad (1)$$

The proportionality coefficient K, called the *velocity constant* of the given reaction, depends on the nature of the reacting substances and the temperature; it does not depend on the concentration of the reacting substances. The velocity constant of a given reaction is a constant value at a given temperature. From equation (1) it can be seen that it is numerically equal to the rate of the given reaction when the concentration of each reactant is 1 mole per litre.

4. Principle of Dynamic Equilibrium

Many chemical reactions do not go to an end because the reaction products obtained react with each other to form the original substances once more. Such reactions are called *reversible.*

An example of a reversible reaction is the reaction of zinc sulphate with hydrogen sulphide. The zinc sulphide and sulphuric acid obtained react to reform zinc sulphate and

hydrogen sulphide:

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4$$

In reversible reactions two processes occur simultaneously but in opposing directions. Therefore, in equations for such reactions two oppositely directed arrows are used instead of the equal mark.

The reaction between the original materials is called the *forward reaction*; that between the resulting products, the *reverse reaction*.

The rate of the forward reaction depends on the concentration of the original materials; the rate of the reverse reaction, on the concentration of the resulting products.

In the beginning of a reversible reaction the forward reaction proceeds with the maximum speed and the rate of the reverse reaction is equal to zero. As the reaction proceeds, the forward reaction slows down because the concentration of the original materials becomes less; the reverse reaction, on the contrary, speeds up as the concentration of the products formed increases. Finally there comes a moment when the reactions in both directions are going on with equal speeds.

The state of a system in which the speed of the forward and reverse reactions are equal is called chemical equilibrium.

Chemical equilibrium is a dynamic (i.e., moving) equilibrium. Both the forward and reverse reactions are constantly going on with equal speeds.

Thus, at equilibrium, chemical reaction between the substances does not stop but proceeds just as fast one way as the other.

Let us consider the reversible reaction

$$A + B \rightleftarrows C + D$$

If we denote the rate of the forward reaction as u_1, the rate of the reverse reaction as u_2, the molar concentrations of the reactants at the moment of equilibrium as [A] and [B], and that of the reaction products at the moment of equilibrium as [C] and [D], the rate of the forward reaction will be $u_1 = K_1[A][B]$ and that of the reverse reaction $u_2 = K_2[C][D]$ (where K_1 and K_2 are the velocity constants of the forward and reverse reactions, respectively).

At the moment of chemical equilibrium the rate of the forward and reverse reactions are equal. Consequently,

$$u_1 = u_2 \text{ and } K_1 [A] [B] = K_2 [C] [D]$$

We may transpose this so that

$$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

The ratio of the two constants K_1 and K_2 is also a constant value. Let us call it the equilibrium constant and denote it as K:

$$K = \frac{[C][D]}{[A][B]}$$

For the reaction

$$mA + nB \rightleftarrows pC + qD$$

the equilibrium constant is

$$K = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

The equilibrium constant is the product of the molar concentrations of the reaction products divided by the product of the molar concentrations of the reactants, each concentration raised to the power indicated by the number of molecules in the balanced equation, when equilibrium has been established in the system.

For example, the reaction for the formation of ammonia from its elements is expressed by the equation

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

The equilibrium constant for this reaction is equal to

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

Like the velocity constant, the equilibrium constant does not depend on the concentrations of the reactants, but varies with the temperature. For a given reaction the equilibrium constant has a definite value for different temperatures. On changing the conditions of the reaction, the chemical equilibrium is disturbed and changes take place in the system until the reaction reaches equilibrium under the new conditions. The equilibrium is then shifted in one or the other direction.

5. Use of the Law of Mass Action in Analytical Chemistry

Of great significance in chemical analysis is the change in concentration of the reactants. An increase (or decrease) in the concentration of one of the original substances results in an increase (or decrease) in the concentration of the reaction products. A change in the concentration of one of the products resulting from the reaction has the opposite effect.

Let us consider the following reversible reaction:

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4$$

$$\text{The equilibrium constant } K = \frac{[ZnS][H_2SO_4]}{[ZnSO_4][H_2S]}$$

If one of the original substances is added after equilibrium is reached, for example $ZnSO_4$, the equilibrium will be disturbed. The denominator of the fraction is increased and the value of K becomes less. In order to keep the value of K constant, it is necessary to increase the numerator. Similarly, the addition of one of the reaction products, for example H_2SO_4, has the opposite effect. The equilibrium constant remains unchanged, only if the concentrations of all the reacting substances are changed. Hence, in order to transform a greater amount of one of the original substances (for example, $ZnSO_4$), it is necessary to add an excess of the reagent that does this; in our case the reagent is H_2S.

CHAPTER III

Ionic Theory

6. Electrolytic Dissociation

Substances whose aqueous solutions conduct an electric current are called *electrolytes*. Such substances are acids, bases, and salts which on dissolving in water break up into ions.

The process of dissociation of an electrolyte into ions on dissolving in a suitable solvent is called *electrolytic dissociation*.

Atoms or groups of atoms carrying electrical charges are called *ions*.

Every electrolyte in aqueous solution breaks up into two kinds of ions: *cations*, positively charged ions, and *anions*, negatively charged ions. The sum of the charges of the cations in a given solution is always equal to the sum of the charges of the anions.

The properties of ions differ from those of the atoms of the respective elements. Thus, sodium ions do not decompose water, whereas sodium atoms decompose water to form sodium hydroxide and hydrogen. Substances containing chloride ions are odourless and colourless, whereas chlorine gas is greenish-yellow and has a pungent smell. Each ion has its individual properties. The properties of cations do not depend appreciably on the properties of the anions in the compounds containing these ions.

The charge carried by an ion is equal to its valency: monovalent ions carry one charge; divalent, two charges, etc. Ions are denoted by the same chemical symbols as atoms. If an ion carries a positive charge, a plus sign is added at the top to the right of the chemical symbol; a negative charge is denoted by a minus sign. Examples: Na^+, Cl^-.

If the number of charges is greater than 1, two or more positive or negative signs are added (for example, Mg^{++}, Al^{+++}, SO_4^{--}, Ba^{++}); it is also designated by the appropriate number in front of the positive or negative sign of the charge (for example, Mg^{2+}, Al^{3+}, SO_4^{2-}, Ba^{2+}).

The process of dissociation is expressed as follows:

$$BaCl_2 \rightarrow Ba^{++} + 2Cl^- \text{ or } BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$$

$$Al_2(SO_4)_3 \rightarrow 2Al^{+++} + 3SO_4^{--} \text{ or } Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$$

The majority of ions in aqueous solutions are combined with water (hydrated). Therefore, in aqueous solutions there are present not simple ions, for example, Al^{3+}, Cl^-, but the hydrated ions $[Al(H_2O)_n]^{3+}$; $[Cl(H_2O)_n]^-$. The hydrogen ion in aqueous solutions is also hydrated, usually with one molecule of water, $[H(H_2O)]^+$ or $[H_3O]^+$. It is called the hydroxonium ion. The hydrated water is not shown for the sake of simplicity (for instance, Al^{3+}, Cl^-, H^+). When reference is made to the hydrogen ion in aqueous solution, it is the hydroxonium ion $[H_3O]^+$ that is implied.

7. Dissociation of Acids, Bases, and Salts

DISSOCIATION OF ACIDS

According to the theory of electrolytic dissociation, an acid is a substance which in aqueous solution yields the hydrogen ion, H^+, as the only cation.

Monobasic acids dissociate into ions in one stage. For example:

$$HCl \rightleftharpoons H^+ + Cl^-; \quad CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Dibasic acids dissociate into ions in two stages. The first stage of the dissociation, as a rule, is much stronger than the second:

$$\text{first stage: } H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$\text{second stage: } HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

As a result of the first stage of dissociation of H_2SO_4, H^+ ions and hydrosulphate ions pass into the solution; as a result of the second stage, hydrogen ions and sulphate ions, SO_4^{2-}. Consequently, there are three types of ions in an H_2SO_4 solution: H^+, HSO_4^-, and SO_4^{2-}.

Tribasic acids dissociate in three stages. The first stage is much stronger than the second; the second stronger than the third. For example, dissociation of phosphoric acid proceeds as follows:

first stage: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ (dihydrophosphate ion)

second stage: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ (hydrophosphate ion)

third stage: $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ (phosphate ion)

An aqueous solution of phosphoric acid contains hydrogen ions, H^+, dihydrophosphate ions, $H_2PO_4^-$, hydrophosphate ions, HPO_4^{2-}, and phosphate ions, PO_4^{3-}; the number of $H_2PO_4^-$ ions is greater than the number of HPO_4^{2-} ions and the number of HPO_4^{2-} ions is greater than the number of PO_4^{3-} ions. The latter are present in an insignificant quantity.

DISSOCIATION OF BASES

A base, according to electrolytic dissociation theory, is a substance which in aqueous solution yields the hydroxyl ion, OH^-, as the only anion.

The dissociation of a base can be expressed, for instance, by the following equations:

$$NaOH \rightarrow Na^+ + OH^-; \quad Ba(OH)_2 \rightleftarrows Ba^{2+} + 2OH^-$$

DISSOCIATION OF WATER

Water dissociates in accordance with the equation

$$H_2O \rightleftarrows H^+ + OH^-$$

Thus, water displays the properties of an acid (forming H^+ ions) and those of a base (forming OH^- ions).

Substances that dissociate both as acids and as bases are called *amphoteric substances* or *ampholytes*. Such compounds include the hydroxides of some metals, which react both with acids and bases. Their dissociation proceeds as bases and as acids; for example, zinc hydroxide, $Zn(OH)_2$, dissociates as follows:

$$Zn(OH)_2 \rightleftarrows Zn^{2+} + 2OH^- \text{ (dissociates as a base)}$$

$$H_2ZnO_2 \rightleftarrows 2H^+ + ZnO_2^{2-} \text{ (dissociates as an acid)}$$

Thus, a $Zn(OH)_2$ solution contains Zn^{2+} ions, OH^- ions, H^+ ions, and ZnO_2^{2-} ions.

DISSOCIATION OF SALTS

Neutral salts, on dissolving in water, dissociate to form metallic ions and acid radical ions:

$$KNO_3 \rightleftarrows K^+ + NO_3^-$$

$$Al_2(SO_4)_3 \rightleftarrows 2Al^{3+} + 3SO_4^{2-}$$

Dissociation of acid salts proceeds in two stages:

$$\text{first stage:} \quad KHSO_4 \rightleftarrows K^+ + HSO_4^-$$

$$\text{second stage:} \quad HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$$

As can be seen, a solution of an acid salt contains hydrogen cations (as a result of dissociation in the second stage) and metallic cations (unlike acids that contain only hydrogen ions).

Dissociation of basic salts. A basic salt is a salt that contains one or several hydroxyl groups. Such a salt disso-

ciates in two or more stages. For example:

first stage: $Mg(OH)Cl \rightleftarrows Mg(OH)^+ + Cl^-$
second stage: $Mg(OH)^+ \rightleftarrows Mg^{2+} + OH^-$

A solution of a basic salt contains OH^- anions (as the result of dissociation in the second stage) and acid radical anions.

If the hydrogen atoms in a polybasic acid are replaced by ions of two different metals, the compounds formed are called double salts. Examples of such salts are: aluminium potassium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$; Rochelle salt (sodium potassium tartrate), $NaKC_4H_4O_6$; sodium ammonium phosphate, $Na_2NH_4PO_4$. These salts dissociate as follows:

$$KAl(SO_4)_2 \rightarrow K^+ + Al^{3+} + 2SO_4^{2-}$$
$$NaKC_4H_4O_6 \rightarrow Na^+ + K^+ + C_4H_4O_6^{2-}$$
$$Na_2NH_4PO_4 \rightarrow 2Na^+ + NH_4^+ + PO_4^{3-}$$

As can be seen from the above equations, aqueous solutions of double salts contain cations of two metals or of a metal and ammonium.

There are also *complex salts*. For example: $K_4[Fe(CN)_6]$; $K_3[Fe(CN)_6]$; $[Ag(NH_3)_2]Cl$.

On dissociating they form simple and complex ions:

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$
$$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Aqueous solutions of complex salts do not contain ions of the constituent elements that make up the complex ion. Thus, in a solution of the salt $K_4[Fe(CN)_6]$ there are no Fe^{2+} and CN^- ions, but only complex $[Fe(CN_6)]^{4-}$ ions.

Review Questions

1. Define the term *ion*.
2. Do the chemical and physical properties of ions and atoms of the same elements differ from each other?
3. Compare the properties of copper ions with those of copper atoms; of iodide ions with those of iodine.
4. Define the terms *cation* and *anion*.
5. What ions are present in solutions of carbonic acid, H_2CO_3, sodium phosphate, Na_3PO_4, and sodium hydrophosphate, Na_2HPO_4?
6. What ions are present in a solution of the double salt ammonium ferric sulphate, $NH_4Fe(SO_4)_2$?
7. Give the equation for the dissociation of the complex salt $K_3[Fe(CN)_6]$.

8. Degree of Dissociation

Electrolytes may be strong or weak. Strong electrolytes on dissolving in water completely dissociate into ions. Weak electrolytes do not dissociate completely into ions; part of the molecules remain undissociated.

Consequently, a solution of a weak electrolyte contains ions and undissociated (unionized) molecules. For example, in a 0.1 *N* sulphurous acid solution containing 0.05 mole of H_2SO_3 per litre, only 20 per cent of the molecules dissociate into ions and 80 per cent remain unionized.

The degree of dissociation is the ratio of the concentration of the dissociated molecules to the total concentration in solution. The degree of dissociation indicates the fraction of the total number of molecules in solution which is dissociated. The degree of dissociation is denoted by the Greek letter α (alpha) and is expressed by the fraction

$$\alpha = \frac{\text{concentration of the dissociated part of the electrolyte}}{\text{total concentration of the electrolyte in solution}}$$

or

$$\alpha = \frac{\text{concentration of molecules dissociated into ions}}{\text{total concentration of molecules in solution}}$$

Since the concentration can be expressed in moles per litre, then

$$\alpha = \frac{\text{number of gram-molecules dissociated into ions}}{\text{number of gram-molecules in solution}}$$

Hence, the degree of dissociation of a 0.05 *M* H_2SO_3 solution is equal to

$$\alpha = \frac{0.01}{0.05} = 0.2$$

The degree of dissociation is expressed by a fraction whose value lies between unity (all the molecules are dissociated into ions) and zero (all the molecules are undissociated). The degree of dissociation can also be expressed in per cent. In the example given above, the degree of dissociation in per cent is equal to

$$\frac{0.01 \times 100}{0.05} = 20\%$$

When it is stated that acetic acid in a 0.1 *M* solution is dissociated by 1.3 per cent, it means that the degree of dissociation is 0.013 and that 1 litre of solution contains $0.1 \times 0.013 = 0.0013$ dissociated moles of acetic acid.

9. Classification of Electrolytes According to Degree of Dissociation

The strength of acids and bases, as that of electrolytes in general, is determined by the degree of dissociation. Acids and bases are classified as strong or weak ones.

Solutions of strong acids are almost completely dissociated, i.e., they contain a great number of hydrogen ions; solutions of weak acids, at an equal concentration, contain few ions.

Strong acids include $HClO_4$, HNO_3, HCl, HBr, HI, H_2SO_4. Such acids as HNO_2, H_2S, H_3BO_3, H_2CO_3, and almost all the organic acids are weak acids. H_3PO_4 and H_2SO_3 are acids of medium strength.

Strong bases dissociate almost completely in aqueous solution, i.e., their solutions contain many hydroxyl ions solutions of weak bases contain few ions.

Strong bases include NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, whereas NH_4OH and the majority of hydroxides of bivalent metals as well as all organic bases are weak bases.

Water is a very weak electrolyte. It produces an equal number of H^+ and OH^- ions in a very small quantity equal to 10^{-7} g-ion/lit.

Most salts are strong electrolytes.

Salts formed by weak acids and strong bases (for example, sodium acetate, CH_3COONa), salts formed by weak bases and strong acids (for example, ammonium chloride, NH_4Cl), and salts formed by weak acids and weak bases (for example, ammonium carbonate, $(NH_4)_2CO_3$) are completely dissociated into ions, just as salts formed by strong acids and strong bases.

Salts that are considered to be insoluble in water are in fact soluble to a very slight degree. Their solutions are always very dilute and do not contain undissociated molecules; they contain only free ions, although their number is insignificant.

Review Questions

1. Define *degree of dissociation.*
2. What electrolytes are called strong and what electrolytes are called weak?
3. What determines the strength of an acid or base?
4. Name all the strong acids and bases you know.
5. Give an example of a weak acid and a weak base.
6. What solution, CH_3COOH or CH_3COONa, contains a greater number of CH_3COO^- ions at an equal molar concentration? Explain why.

10. Influence of Conditions Upon Degree of Dissociation of Weak Electrolytes

The extent to which an electrolyte dissociates depends on several conditions.

1. A change in temperature, although only slightly, affects the degree of dissociation: in the case of certain electrolytes it increases with a rise in temperature; in other electrolytes, it decreases.

2. The degree of dissociation of electrolytes depends largely on its concentration in the solution. The closer to each other the cations and anions of the dissolved electrolyte in the solution, the greater their attraction to each other. The distance between the ions depends on the concentration of the solution. Hence, with an increase in concentration, the degree of dissociation drops and vice versa. In more concentrated solutions the degree of dissociation is less than in dilute solutions, i.e., the degree of dissociation increases with dilution of solutions with water. On considerable dilution, dissociation is practically complete.

3. If a solution contains two electrolytes that have one and the same ion, it is said that they have a common ion; for example, in a solution containing HCl and KCl, the Cl^- ion is common to both, and in a solution of CH_3COOH and CH_3COONa, the CH_3COO^- ion is the one contained in common. When solutions of two electrolytes with a common ion, having the same degree of dissociation and the same concentration in gram-equivalents per litre, are mixed, the degree of dissociation of each electrolyte will remain unchanged.

4. If a salt of a weak acid is added to a solution of the acid, the degree of dissociation of the weak acid is considerably

reduced. Let us see how the degree of dissociation of acetic acid will change, for example, on adding a 0.1 *M* sodium acetate solution to a 0.1 *M* CH_3COOH solution ($\alpha = 1.3$ per cent) in which the salt is completely dissociated:

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$
$$CH_3COONa \rightleftarrows Na^+ + CH_3COO^-$$

On adding sodium acetate to the acetic acid solution, the concentration of CH_3COO^- ions is increased. As a result of this, the equilibrium of dissociation of the acid is shifted to the left, i.e., in the direction of formation of undissociated CH_3COOH molecules. By sufficiently increasing the concentration of CH_3COO^- ions, the dissociation of CH_3COOH can be almost completely suppressed.

Hence, the degree of dissociation of a weak acid is decreased if a strong electrolyte with a common ion is added to the acid solution, even when the strong electrolyte is added in a small quantity. If a large quantity of a strong electrolyte is added, the weak electrolyte becomes practically undissociated.

It follows from this that a weak acid in the presence of its salt or a strong acid does not appreciably dissociate into ions. The same is true for a weak base, the dissociation of which is depressed in a strongly alkaline medium or in the presence of a salt with a common cation.

Review Questions

1. What conditions affect the degree of dissociation of electrolytes?
2. How will the concentration of hydrogen ions change on diluting a concentrated solution of HCl with water?
3. How will the concentration of hydroxyl ions in a NH_4OH solution change on adding NH_4NO_3 to it?

11. Dissociation Constant

The dissociation of an electrolyte is a reversible process. The concentration of ions and that of undissociated molecules are interdependent. A solution of acetic acid, CH_3COOH, for example, contains undissociated CH_3COOH molecules, H^+ ions, and acetate, CH_3COO^-, ions. If we

denote the concentration of hydrogen and acetate ions in gram-ions per litre as $[H^+]$ and $[CH_3COO^-]$, respectively, and the concentration of undissociated molecules in moles per litre as $[CH_3COOH]$ and apply the law of mass action to the process of dissociation, we will obtain the following expression for the equilibrium constant, which in this case is called the dissociation constant:

$$K_{CH_3COOH} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The dissociation constant at a given temperature is invariable. If the concentration of $[H^+]$ ions or $[CH_3COO^-]$ ions is changed in a CH_3COOH solution, the concentration of undissociated CH_3COOH molecules will change accordingly, but the ratio $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ will remain constant at a given temperature.

The dissociation constant of a given electrolyte is equal to the product of the concentrations of the ions in solution divided by the concentration of the undissociated molecules of this electrolyte.

The degree of dissociation changes with the concentration of the electrolyte; the dissociation constant of an electrolyte remains unchanged at a given temperature. This applies only to dilute solutions of weak electrolytes.

The total number of dissolved molecules is taken in the denominator when determining the degree of dissociation, whereas only the number of undissociated molecules is taken in the denominator when determining the dissociation constant. Hence, only the degree of dissociation depends on the concentration of the electrolyte.

In a binary electrolyte, i.e., an electrolyte that dissociates into two ions of the same valency, for example, acetic acid whose aqueous solution contains H^+ ions and CH_3COO^- ions, the dissociation constant is expressed by the equation

$$K_{CH_3COOH} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad (1)$$

If we denote the concentration of the electrolyte (in this case acetic acid) as C, and the degree of dissociation as α, then the number of moles of dissociated molecules in

solution will be $C\alpha$ and the number of moles of undissociated molecules will be $C - C\alpha$. Each dissociated molecule of a binary electrolyte produces one $[H^+]$ cation and one $[CH_3COO^-]$ anion, i.e., the concentration of H^+ ions and that of CH_3COO^- ions is equal to the number of moles of dissociated molecules, $C\alpha$.

Substituting these values in equation (1), we have

$$K = \frac{C\alpha \cdot C\alpha}{C - C\alpha} \quad \text{or} \quad K = \frac{C\alpha^2}{1 - \alpha} \tag{2}$$

Equation (2) is the expression for Ostwald's dilution law. It gives the relationship between the degree of dissociation and the concentrations of weak electrolytes. The degree of dissociation decreases with an increase in concentration and increases with a decrease in concentration, since at a given temperature K is a constant value. For very weak electrolytes, for which the degree of dissociation is very small, the denominator in equation (2) can be taken as equal to 1. Then

$$K = C\alpha^2 \quad \text{and} \quad \alpha = \sqrt{\frac{K}{C}}$$

Hence, on diluting a solution, the degree of dissociation increases with a decrease in the concentration of the solution C. Experiments confirm this conclusion.

Review Questions

1. Define the term *dissociation constant.*
2. On what conditions does the dissociation constant depend?
3. For what electrolytes can the dissociation constant be calculated?
4. What is the equation for Ostwald's dilution law?

CHAPTER IV

Chemical Reactions in Aqueous Solutions

12. Ionic Reactions

All reactions in aqueous solution take place between ions. Thus, chloride ions present in all chloride solutions, on coming in contact with Ag^+ ions, precipitate silver chloride; whereas the chlorine in organic compounds, where

it is not in the form of an ion (for example, chloroform, $CHCl_3$), does not produce any precipitate.

Neither does potassium chlorate, $KClO_3$, precipitate silver chloride, because it dissociates according to the equation

$$KClO_3 \rightleftarrows K^+ + ClO_3^-$$

from which it can be seen that a $KClO_3$ solution contains the complex ion ClO_3^- and not the Cl^- ion.

In addition to the molecular form, use is made of another form of chemical equation, the ionic form, which is more suitable for representing reactions that actually take place in aqueous solutions.

For example, the equation for the reaction between hydrochloric acid and silver nitrate[1] in the molecular form is

$$HCl + AgNO_3 = AgCl\downarrow + HNO_3$$

If the dissociated substances are presented in the form of ions, the equation in the complete ionic form will be

$$Ag^+ + NO_3^- + H^+ + Cl^- = AgCl\downarrow + H^+ + NO_3^-$$

On cancelling like ions occurring on both sides of the equation (H^+ and NO_3^-) we obtain an equation in the reduced ionic form:

$$Ag^+ + Cl^- = AgCl\downarrow$$

It can thus be seen that if a solution contains silver ions and chloride ions, they unite to form molecules of silver chloride.

The equation in the reduced ionic form is simpler and more general than the corresponding equation in the molecular form. From the reduced ionic equation given above it is clear that not only hydrochloric acid but any soluble chloride (NaCl, $BaCl_2$, $AlCl_3$, etc.) precipitates AgCl from a solution of any soluble silver salt ($AgNO_3$, $AgNO_2$).

At the beginning of a course in analytical chemistry, every reaction should be written in the notebook in the form of three equations: (a) as a molecular equation in which the reacting and resulting substances are presented in the molecular form, and the formula of the insoluble substances (precipitates) obtained are marked by an arrow

[1] An arrow pointing downwards shows that the substance is precipitated; an arrow pointing upwards, that the substance evaporates.

(↓); (b) as a complete ionic equation in which reacting and resulting strong electrolytes are given in the form of ions, and weak electrolytes (water, weak acids, weak bases) and sparingly soluble compounds (for instance, $BaSO_4$, AgCl) are written in the form of undissociated molecules; (c) as a reduced ionic equation in which only the ions and compounds that take part in the reaction are indicated. For example, the reaction between sodium sulphate and barium chloride should be expressed by the following three equations:

(a) $Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl$

(b) $2Na^+ + SO_4^{2-} + Ba^{2+} + 2Cl^- = BaSO_4\downarrow + 2Na^+ + 2Cl^-$

(c) $Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$

Exercises

Write the equations in the three forms for the reactions between the following substances:

(a) potassium chloride and silver nitrate;
(b) ammonium hydroxide and sulphuric acid;
(c) sodium hydroxide and acetic acid;
(d) sodium acetate and sulphuric acid;
(e) phosphoric acid and ammonia;
(f) potassium phosphate and nitric acid.

13. Direction of Chemical Reactions in Aqueous Solutions

Two kinds of chemical reactions take place in aqueous solutions of electrolytes: direct combination and oxidation-reduction (see Chapter XII).

The reaction of direct combination in aqueous solutions, as has already been pointed out, consists in the ions uniting with each other to form molecules. Let us investigate what ions of various electrolytes combine with each other and what ions do not.

Ionic reactions always proceed in the direction of a decrease in the number of free ions in the solution. Below are given several examples of such reactions.

1. Of great importance in analytical chemistry is the formation of precipitates, i.e., compounds that are only very slightly soluble in water. Precipitation occurs when

ions unite to form sparingly soluble chemical compounds. For example, on mixing solutions of barium salts and sulphates, a practically insoluble salt, barium sulphate, is always precipitated:

$$SO_4^{2-} + Ba^{2+} = BaSO_4\downarrow$$

2. Acids react with alkalies (neutralization); hydrogen ions on colliding with hydroxyl ions combine to form water, a compound that is only slightly dissociated:

$$H^+ + OH^- = H_2O$$

3. When hydrochloric acid reacts with sodium acetate solution, the hydrogen ions of the hydrochloric acid combine with the acetate ions, CH_3COO^-, to form slightly dissociated acetic acid:

$$HCl + CH_3COONa = NaCl + CH_3COOH$$
$$H^+ + Cl^- + Na^+ + CH_3COO^- = Na^+ + Cl^- + CH_3COOH$$
$$H^+ + CH_3COO^- = CH_3COOH$$

4. When ammonium salts react with an alkali hydroxide, the ammonium ions, on colliding with the hydroxyl ions in the solution, combine with the latter to form a sparingly soluble base, ammonium hydroxide:

$$NH_4Cl + NaOH = NH_4OH + NaCl$$
$$NH_4^+ + Cl^- + Na^+ + OH^- = NH_4OH + Na^+ + Cl^-$$
$$NH_4^+ + OH^- = NH_4OH$$

In aqueous solutions, ions combine with each other when a precipitate, water, a weak acid, or a weak base is formed.

A course in inorganic chemistry studies, in addition to direct combinations, other types of chemical reaction: simple decompositions, single and double replacements. Decomposition takes place in an aqueous solution when the ions unite to form unstable compounds. Examples are:

(a) $2H^+ + CO_3^{2-} = H_2CO_3$ (direct combination)

$H_2CO_3 = H_2O + CO_2\uparrow$ (simple decomposition)

(b) $NH_4^+ + OH^- = NH_4OH$ (direct combination)

$NH_4OH = NH_3 + H_2O$ (simple decomposition)

Double replacement, for example,

$$AgNO_3 + KCl = AgCl\downarrow + KNO_3$$

is, at the same time, a direct combination of ions:

$$Ag^+ + Cl^- = AgCl\downarrow$$

Single replacement is, simultaneously, an oxidation-reduction reaction (see Chapter XII).

$$CuSO_4 + Zn = ZnSO_4 + Cu$$
$$Cu^{2+} + Zn = Cu + Zn^{2+}$$

Exercises

Write the equations only for those reactions in which ions unite with each other:

(a) sodium sulphate plus potassium hydroxide; (b) sodium hydrophosphate plus sodium hydroxide; (c) sodium dihydrogen phosphate plus ammonium hydroxide; (d) potassium nitrate plus sulphuric acid; (e) potassium nitrite plus sulphuric acid; (f) barium hydroxide plus sodium hydroxide; (g) ammonium nitrate plus potassium hydroxide.

CHAPTER V

Laboratory Work in Qualitative Analysis

14. Chemical Methods of Qualitative Analysis

Chemical analysis of a substance is carried out, in the main, in two ways: by the dry method in which the substance under test is not dissolved, and by the wet method in which the substance under test is first dissolved and then analyzed to determine its composition. The dry method is usually used in preliminary tests in the laboratory or in geological investigations in field conditions. In analysis by the dry method, the following special laboratory procedures are employed:

1. **Flame tests.** The sample is tested for coloration of the flame, since certain elements that form volatile compounds give the flame a characteristic colour; for example, barium—yellow-green, sodium—yellow.

2. **Bead tests.** A small quantity of the substance under test on being fused with borax, hydrated sodium borate ($Na_2B_4O_7 \cdot 10H_2O$), or ammonium dihydrogen phosphate ($NH_4H_2PO_4 \cdot 4H_2O$) produces a glass bead of a colour that is characteristic of the given ion. For example, cobalt salts give blue beads; chromium salts, green beads.

3. Blowpipe analyses. The substance under test is heated on a charcoal block with the aid of a blowpipe as a result of which a coloured sublimate is deposited. For example, lead yields a yellow deposit; arsenic, a white deposit.

In analysis by the wet method, the substance under test is first dissolved in water or in an acid or alkali solution. If it does not dissolve in water or an acid or alkali solution, it should be fused with a solid alkali or a mixture of sodium carbonate and potassium carbonate and the fusion obtained dissolved in water or in an acid (depending on the substance).

Analytical reactions are carried out by introducing into the solution under test appropriate reagents which react with the ion being detected to produce a characteristic reaction product. Such reactions are called *characteristic reactions* or *identification tests* for the given ion.

In qualitative analysis use is made of characteristic reactions which yield precipitates of specific properties, colour, and form; coloured soluble compounds; or gaseous products. For example, the chloride ion reacts with the silver ion to produce a white curdy precipitate of silver chloride that is insoluble in nitric acid but is soluble in ammonia solution. Hence, silver nitrate in a nitric acid medium is a characteristic reagent for identifying the chloride ion. Under certain conditions ferric ions react with thiocyanate ions to form a red-coloured compound that is soluble in water. The sulphides of many metals react with acids to yield hydrogen sulphide, a gas with a specific odour. Alkalies react with ammonium salts, on heating, to produce ammonia.

Identification tests can be conducted by test-tube, spot, and microscopic (microcrystalloscopic) analysis.

In the test-tube method, a certain amount of a reagent is added to a sample of the solution under test in a test tube and the results of the reaction are observed. If a precipitate is formed, note is taken of its appearance (amorphous or crystalline). If a crystalline precipitate is formed, it is analyzed by the microcrystalloscopic method. In this method a drop of the solution under test is mixed with a drop of the reagent (sometimes taken in the dry form) on a slide and the crystals obtained are observed under a microscope.

Colour reactions, i.e., those that are accompanied by a change in colour of the solution or the formation of a coloured precipitate, are carried out in test tubes or by spot tests. These tests were first proposed by Professor N. A. Tananaev. Spot tests are carried out on strips of filter paper or on porcelain spot plates. The presence of certain ions in the solution is indicated by the colour of the resulting spot, the arrangement of coloured rings on the filter paper, or the characteristic colour of the solution or precipitate obtained on the spot plate.

Depending on the amount of substance taken for analysis, investigation is carried out by means of macro analysis, semimicro analysis, micro analysis, or ultramicro analysis.

In ordinary qualitative macro analysis, about 500 mg or from 20 to 100 ml of solution are taken for the analysis; this makes it possible to detect from 1 to 5 mg of ions present in solution. In micro analysis, which requires special apparatus, 1 mg of the substance under test is analyzed. Recently, methods of ultramicro analysis have been developed in which from 10^{-3} to 10^{-9} mg of substance or from 10^{-3} to 10^{-6} ml of solution is taken for the tests.

In semimicro analysis from 10 to 100 mg of the substance under test or 0.5 to 0.8 ml of solution are taken for analysis. This method has all the merits of classical macro analysis and, in addition, some advantages over it, namely: work with small quantities of the substance under test makes it possible to reduce the amount of reagent used and the time spent on carrying out the analysis, as well as to improve the sanitary and hygienic working conditions. The procedures and techniques of semimicro analysis demand great accuracy and care during the process of work. Semimicro analysis is now aknowledged to be the most suitable and economical method of analytical chemistry. This textbook describes semimicro analysis only for qualitative analysis.

15. Apparatus for Semimicro Analysis

In the semimicro method of qualitative analysis use is made of the following apparatus: test tubes, beakers, evaporating dishes, crucibles, spot plates, watch glasses, slides, gauze, water baths, burners, electric hot plates, centrifuges.

Test tubes. Most analytical operations are conducted in test tubes. Two kinds of test tubes are used: centrifuge tubes (see Fig. 1*a*) used mainly for centrifuging; and 5-10 ml cylindrical test tubes (see Fig. 1*b*). Test tubes are washed with special bottle brushes. First empty the test tube of its contents and wash it 2 or 3 times with tap water, then pour a little water into it and clean the walls and bottom of any adhering particles by means of a bottle brush. After that wash the test tube with tap water and finally 2 or 3 times with distilled water. The clean test tubes are kept in a wooden or plastic test-tube rack.

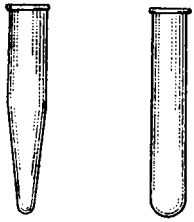

Fig. 1. Test tubes
a — centrifuge; *b* — cylindrical

Dropper pipette. This is a glass tube the lower end of which is drawn out to a fine capillary (see Fig. 2). At the top it is fitted with a rubber bulb or tube (teat) that is tightly stoppered with a glass ball or a piece of fused glass rod. The pipette is 80-90 mm long and of a capacity of approximately 1 ml. An ordinary medical eye dropper can be used instead of a capillary pipette. The solution is drawn into the pipette by pressing and then releasing the rubber teat. The pipette should be washed 2 or 3 times with distilled water each time after it is used.

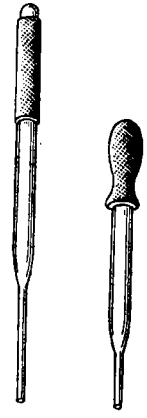

Fig. 2. Dropper pipettes

Reagent bottles. Reagents are kept in 20-30 ml bottles provided with ground-glass covers carrying small pipettes (see Fig. 3). Ordinary 20-30 ml bottles are also used for this purpose. They are stoppered with pipettes that nearly reach the bottom of the bottle. The rubber teat of the pipette must be of such a diameter that it can serve as a stopper for the bottle. All the reagent bottles should bear labels denoting the name or formula of the substance contained in it.

Bottles containing reagents should be kept in a special wooden block (see Fig. 4) or on a shelf above the workplace.

When working with reagents, the bottles should not be removed from their place in the block. Reagents should be taken only with the pipette designated for the given bottle. The pipette should not come in contact with the walls of

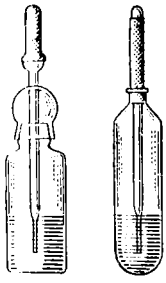

Fig. 3. Reagent bottles

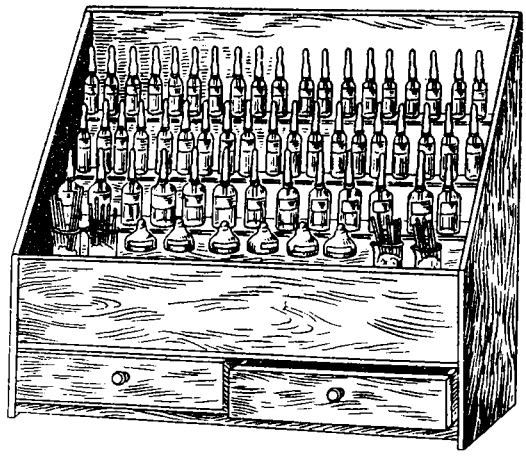

Fig. 4. Reagent block for semimicro analysis

the test tube in order to avoid contamination. It is recommended that concentrated acids, ammonia solutions, and other volatile substances be kept in glass dropping bottles with ground-glass stoppers.

In addition to the solutions of the main reagents that are used frequently, the laboratory should be provided with a set of special solutions that are seldom used as well as certain dry reagents. The jars with the dry reagents should have stoppers carrying glass rods flattened at the bottom.

Flasks and beakers. In semimicro analysis use is made of 50-100 ml thin-walled chemical flasks and lipped beakers (see Fig. 5).

Wash bottles. A properly made wash bottle is of great importance in analytical work (see Fig. 6). It consists of a 100-150 ml thin-walled, flat-bottomed flask closed with a stopper (preferably a rubber stopper) carrying two glass tubes. One of them is short and is bent at an obtuse angle;

it is used to blow air into the flask and it ends almost directly under the stopper. The other tube is long and extends to the bottom of the flask. The top end of the tube is bent at an angle of 60-70°; the bottom end should be bent so that the end of the bent part nearly touches the bottom of the flask. The top end of this tube is connected by means of a piece of rubber tubing 4-5 cm long to a short glass tube

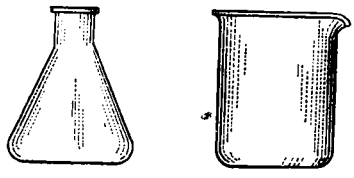

Fig. 5. Flask and beaker

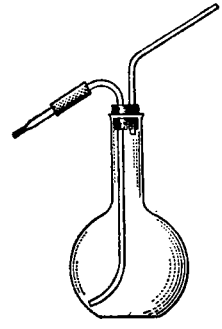

Fig. 6. Wash bottle

with a capillary drawn out at its end. The ends of all the tubes should be flame polished. As the wash bottle is often filled with hot liquids, it is recommended that the bottle neck be wrapped with asbestos cord or coarse thread so that it is convenient to hold it.

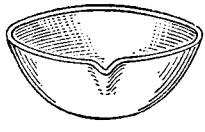

Fig. 7. Evaporating dish

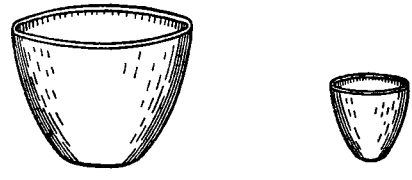

Fig. 8. Porcelain crucibles

Glass stirring rods should be 3-5 mm in diameter and 7-10 cm long. The ends of the rods should be well fused.

Watch glasses are 4-5 cm in diameter.

Evaporating dishes are used for evaporating or heating solutions; their capacity is 5-10 ml (see Fig. 7).

Porcelain crucibles (see Fig. 8) are used for igniting residues, fusing insoluble substances, etc.; they are of a capacity of 3-5 ml.

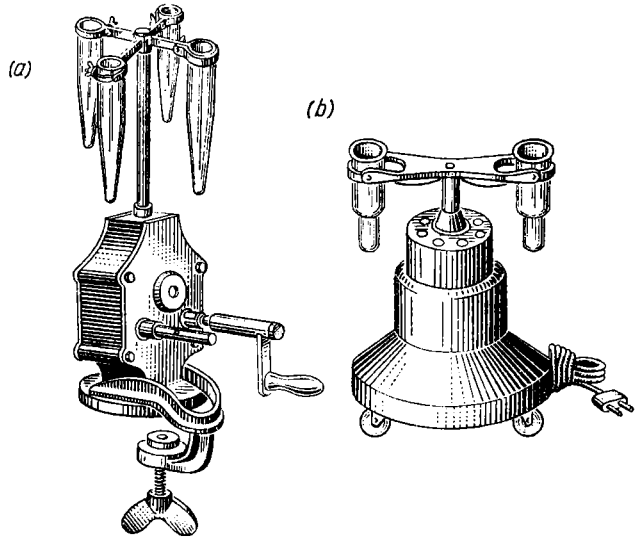

Fig. 9. Centrifuges

Centrifuge (see Fig. 9) is the apparatus used for separating precipitates from the solution. After centrifuging, the clear liquid (supernatant) is decanted while the precipitate is left in the test tube.

Centrifuges may be manually driven (see Fig. 9*a*) or electrically driven (see Fig. 9*b*).

Prior to starting a centrifuge, it is necessary to close the protective lid to avoid any accident.

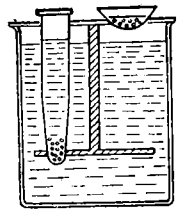

Fig. 10. Water bath

Burners and other laboratory equipment. It is convenient to use microburners in semimicro analysis, but depending on the conditions of the test, ordinary gas burners or alcohol (spirit) lamps can also be used. Iron stands with rings, asbestos gauzes, and water baths (see Fig. 10) are likewise needed to carry out qualitative analysis.

16. Cleaning Chemical Laboratory Ware

The glassware and porcelain ware used in analytical work must be clean. It should be washed immediately after usage. To achieve thorough cleaning, it is good practice to use a warm concentrated sodium carbonate solution, hot soapy water, a warm alkaline potassium permanganate solution, or the chromic-sulphuric acid cleaning solution.

The soap solution is prepared by dissolving small pieces of soap in hot water. The alkaline potassium permanganate solution is prepared by dissolving 5 g of $KMnO_4$ in 100 ml of hot 10 per cent sodium hydroxide solution.

The chromic-acid cleaning solution is prepared as follows. Dissolve 15 g of ground commercial potassium dichromate, $K_2Cr_2O_7$, in 100 ml of hot water. Cool the solution and add 100 ml of concentrated sulphuric acid (commercial acid may be used) drop by drop, stirring constantly. This solution is kept in a bottle with a ground-glass stopper. It is recommended that the bottle containing the chromic-acid cleaning solution be placed on a glass or porcelain plate. A bottle brush should not be used when washing laboratory ware with alkaline potassium permanganate solution or with chromic-acid cleaning solution.

Wet the inner surface of the vessel being cleaned with a small amount of one of the above-mentioned warm cleaning agents. Then wash the vessel 6 or 7 times with tap water to remove traces of the cleaning solution. Each time the cleaning solution is used, pour it back into the respective bottle. The same portion of soap, alkaline potassium permanganate, or chromic-acid cleaning solutions can be reused several times.

Glassware is best washed with the soap solution because the alkaline potassium permanganate solution attacks glass, while great care must be taken when working with the chromic-acid cleaning solution (it can cause burns). If solid particles adhere to the vessel walls, which are not removed by the above cleaning solutions, introduce small pieces of paper into the vessel, add warm water, and vigorously shake up the mixture. The vessel is deemed to be clean if, after pouring off the water, its inner walls are wetted uniformly and no drops of water remain on them.

When a properly washed vessel is turned upside down it seems to be dry. After washing the vessel with tap water, rinse it 2 or 3 times with small quantities of distilled water.

17. General Directions for Laboratory Work

The following rules must be observed when working in a laboratory:

1. Keep the workplace clean and in good order. If any liquid is accidently spilt, immediately wipe it up with a moist rag, wash the table with water, and then wipe it with a dry rag. There should be no unnecessary objects on the workplace; only the vessels, apparatus, and reagents needed for the given test, a textbook of analytical chemistry, and a notebook for recording the test results should be at hand. All records should be made in the notebook—by no means on scraps of paper.

2. Arrange all apparatus, vessels, and reagents on the table so that it is convenient to work with them. After they have been used, put them in place again.

3. Take care that the reagents are not contaminated in any way. Always place the stoppers of reagent bottles on the table upside down. Do not leave the bottles open for a long time. Never close a bottle with the stopper from another bottle. Put each bottle in place after using it. If any reagent taken from a bottle is left over, do not pour it back into the bottle.

4. Do not put used filter paper, residues, broken glass, pieces of paper, matches, etc. in the sink; put them in a special waste pail or box. Do not pour acid and alkali solutions or solutions of mercury compounds in the sink either; pour them into glass jars kept for this purpose.

5. Use only matches to light up burners. When lighting gas burners, avoid letting them strike back. If this should happen, close the stopcock at once and relight the burner only in 1-2 minutes, after reducing the clearance through which the air enters.

6. Be economical when using gas, electricity, and distilled water.

7. Be sure to observe safety rules when using concentrated acids, alkalies, and poisonous substances.

8. All reactions that are accompanied by the evolution of smoke or gases with an unpleasant odour should be conducted under a hood.

9. Before carrying out a test, read the description of the procedure in a textbook. Make sure that you understand why each reagent is added and what reaction takes place on adding it.

10. Prior to using a reagent, read the label on the bottle to make sure that you have taken the required reagent.

11. Always use the specified quantities of the unknown substance and reagents for the given test; for example, in semimicro analysis, not more than 3-5 drops.

12. Record the result of each test in a special laboratory notebook immediately after performing the test. The report should be brief and legibly written. The following data should be recorded: the purpose of the test, the substance under test, the reagent used, the equation for the reaction that takes place and the visible results—the formation of a precipitate, its colour, character (crystalline or amorphous), solubility in water, acids, and alkalies; the change in the colour of the solution; the colour and odour of gases liberated.

13. If the test results are not clear, consult the teacher.

14. Do not change the test procedure without the teacher's approval.

15. Do not leave the precipitate in the test tube after the test is over, but dissolve it and wash the test tube at once.

16. If in the course of the analysis a precipitate or solution must be kept for even a short time, glue a legibly marked label on the vessel containing it.

18. Semimicro Techniques

Heating of solutions. Solutions are heated in test tubes, flasks, or beakers which are placed on an asbestos gauze. The outside of the vessel must be dry, otherwise it may burst. When heating a liquid containing a precipitate, it should be stirred constantly with a glass rod.

A test tube containing a liquid can be heated directly in a burner flame, first passing the tube slowly back and forth

through the flame or just above it (heating only the walls, not the bottom, of the tube). The mouth of the test tube must never be pointed at anybody. It is recommended that test tubes containing both liquids and precipitates be heated in a water bath because when heated directly over a flame, bumping occurs and the mixture can be thrown out of the test tube.

In the course of the test it is frequently necessary to concentrate the solution (reduce its volume) or evaporate it to dryness. Evaporating dishes are used for this purpose; they are placed on an asbestos gauze or in a water bath.

Precipitates are ignited in a porcelain crucible that is heated directly in a burner flame, on an electric hot plate, or in a muffle furnace.

Precipitations. Precipitates may be crystalline or amorphous. Crystalline precipitates (for example, $BaSO_4$, $MgNH_4PO_4$) when examined with the naked eye seem to be either fine or coarse-grained; under a microscope, individual crystals of a specific form are discernible. Crystalline precipitates often fail to appear immediately on combining the solutions of the reacting substances, but are formed only after some time has elapsed. Precipitation can be accelerated by shaking the solution or rubbing a glass rod against the walls of the test tube. Crystalline precipitates accumulate rapidly at the bottom of the vessel and are readily centrifuged. Amorphous precipitates are usually formed at once, on adding the appropriate reagent, but they settle at the bottom of the vessel very slowly and are separated with difficulty by centrifuging. Amorphous precipitates readily form colloidal sclutions. Coagulation is produced by heating and by adding an electrolyte. Amorphous precipitates, according to their appearance, are divided into curdy precipitates (AgCl) and gelatinous precipitates ($Fe(OH)_3$).

Reactions based on the formation of precipitates containing definite ions are conducted in qualitative analysis for two purposes: (a) to detect a given ion, (b) to separate it from the other ions contained in the solution. In the first case it is unnecessary to carry out the test with all of the substance taken for analysis. One drop of the solution under test is often sufficient to determine the presence or absence of a certain ion.

If in the course of the analysis ions must be isolated, it is necessary, first of all, to ascertain the presence of the given ion in the solution. For this purpose to 3-5 drops of the solution under test add a few drops of the appropriate reagent. If the reagent causes a precipitate to form, add it to all of the solution under test in a quantity required for complete isolation of the ions in the form of a compound of low solubility.

Precipitation is preferably conducted in hot solutions because at high temperatures precipitates with larger crystals are formed. Precipitates with large crystals are easily separated by filtration or centrifuging and are easier to wash. The solution of the precipitant used to obtain such precipitates should be added slowly, stirring the mixture constantly with a glass rod.

Precipitation with the aim of isolating particular ions is usually carried out as follows. Pour the required amount of the solution under test into a centrifuge tube or beaker. Read the textbook to learn what the conditions for precipitation are and obtain the proper medium (acidic, alkaline, or neutral solution) and temperature. Test the solution to find out whether it is acidic or alkaline by means of indicator paper. For this purpose place a strip of indicator paper on a clean watch glass, stir the solution under test with a glass rod, and then touch the paper with the tip of the glass rod. If, for example, litmus paper turns red, the solution is acidic; if it turns blue, the solution is alkaline. After that, if necessary, carefully heat the test tube containing the solution over a small burner flame or by dipping it into a boiling water bath for 3-5 minutes. Then, stirring constantly, add the precipitant taken in excess[1] and test for completeness of precipitation (see below).

Centrifugal separations. In semimicro analysis the precipitates are usually separated from the solution by centrifuging. When using a centrifuge it is necessary to observe the following rules:

1. Use tubes of the same size and shape.

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[1] An excess of reagent is the quantity taken over and above the stoichiometric quantity found by calculation.

2. Pour a quantity of the mixture into the tube so that its level is 6-8 mm below the rim in order to avoid penetration of the liquid into the tube case.

3. Balance the tube containing the mixture by a second tube. For this purpose select a second tube equal in weight to the first one. Hold both tubes in the left hand and add water from a beaker into the empty tube until the heights of liquid in both tubes are the same. If the tubes are not balanced properly, the centrifuge begins to 'throb' and the solution may be spilt. Throbbing is detected by the characteristic sound produced.

4. After balancing the tubes, begin centrifuging. When working with a manually driven centrifuge, turn the handle uniformly. When working with an electrically driven centrifuge, first close the lid, then switch on the current and move the rheostat handle slowly to increase the speed of rotation to that required.

5. After completing work, stop the hand centrifuge gradually. Prior to stopping an electric centrifuge, slowly return the rheostat handle to the initial position. When the centrifuge has completely stopped, open the lid and remove the test tube.

6. Never allow the centrifuge to operate without supervision. If any abnormal sound, vibration, or considerable heating is observed, immediately switch off the current or stop turning the handle of a hand-operated centrifuge. An unusual sound may be produced if a tube is broken; vibration shows that the centrifuge tubes are not balanced. If a tube breaks during centrifuging, remove the case, free it from fragments of glass, wash thoroughly with water, and dry with a towel.

Duration of centrifugation depends on the character of the precipitate. Crystalline precipitates separate from the solution rapidly, therefore 0.5-1.5 minutes is sufficient. Amorphous precipitates are slowly compacted; centrifuging is therefore continued for 2-3 minutes. After centrifuging, all of the precipitate usually settles (is caked) at the bottom of the tube and the solution becomes clear; the latter is called the supernatant. Some precipitates rise to the surface or settle very slowly; they cannot be separated by centrifuging but must be filtered.

Test for completeness of precipitation. After centrifuging, without decanting the supernatant clear solution, carefully pour a few drops of the precipitating agent down the walls of the tube. Complete precipitation is attained when no turbidity appears at the place where the drops fall.

In certain cases a change in the concentration of hydrogen ions, i.e., the acidity or alkalinity of the solution, indicates that precipitation is complete. In this case, after thoroughly stirring the mixture and allowing it to settle, wet the end of a glass rod with the solution and touch it to litmus paper. Completeness of precipitation is determined by the change in colour of the indicator paper.

Separation of the supernatant from the precipitate. On centrifuging, the precipitate is caked at the bottom of the tube so compactly that it is possible to pour off the clear solution almost completely. This process is called *decantation.*

Washing of precipitates. After making sure that precipitation is complete, remove the clear liquid by means of a pipette or by decanting, taking care not to stir up the precipitate. Then wash the precipitate with distilled water. If the precipitate is liable to pass over into the colloidal state, add an electrolyte to the distilled water used to wash it. For instance, wash a $Fe(OH)_3$ precipitate with a dilute ammonium nitrate solution.

The quantity of liquid used for washing and the number of washings vary with the volume of the precipitate, its properties, etc. Gelatinous precipitates must be washed a greater number of times than crystalline precipitates. In the latter case 2 or 3 times will be sufficient.

To wash the precipitate, pour a few millilitres of distilled water or other suitable liquid into the centrifuge tube. Hold the tube in an almost horizontal position so that the precipitate is spread over a large surface and stir the mixture thoroughly. Then centrifuge once more and decant the wash water. Repeat this operation 2 or 3 times.

Dissolving of precipitates. To dissolve the washed precipitate, add the appropriate solvent into the centrifuge tube. If from previous tests it is already known that the precipitate should dissolve in the volume of the solvent added, stir the mixture thoroughly, carefully heating the test tube in a water bath or over an open burner flame. If on doing

so the precipitate does not dissolve completely, shake up the contents of the tube thoroughly and transfer the turbid mixture obtained to an evaporation dish or beaker. If it is impossible to transfer all of the precipitate at once, pour a second portion of solvent into the tube and repeat the operation. Stir the mixture in the evaporating dish thoroughly and, if necessary, heat it. Then transfer the mixture to a tube and centrifuge. Separate the clear solution from the precipitate and analyze the supernatant and precipitate separately.

Tests for ions. Ions are detected by using one of the following test methods (see Sec. 14): ordinary test-tube (wet or semi-wet), spot, or microcrystalloscopic method.

19. Laboratory Procedure

Laboratory work in qualitative analysis includes tests for studying the group reactions of ions, practice in analysis of mixtures of a known composition, and control tests (qualitative analysis of a number of mixtures whose composition is unknown to the student). Place the solution or the solid received from the teacher in a previously prepared clean flask (dry from the outside) that has a label glued on it with the inscription "Control. Work for the Determination of Cations (Anions) of Group...". Write your name and the number of your workplace under this inscription.

The results of the control tests should be given to the teacher in written form, for example, as follows:

Name of student

Group or class *Test No.*

Operation No.	Substance	Operation	Reagent used	Observations	Conclusion
1	Solution under test	Determination of NH_4^+ ions	NaOH with heating	Wet litmus paper did not change in colour	NH_4^+ ions are absent
	Supernatant (3)	Determination of Al^{3+} ions	NH_4Cl with heating	A white gelatinous precipitate appears	Al^{3+} ions are present

CHAPTER VI

Analytical Classification of the Cations

20. Cation Groups

In qualitative inorganic analysis, the cations and anions are analyzed separately. For the systematic analysis of mixtures, the solution is first treated successively with carefully selected group reagents to segregate similar cations into groups. Then on further treatment of the precipitates obtained, the cations of each group are separated and identified by suitably characteristic reactions.

The cations are subdivided into five analytical groups each of which has a group precipitant that forms insoluble compounds with all the cations of the group simultaneously. The only exception is Group I for which there is no single reagent (anion) capable of forming precipitates with all the cations of this group at the same time.

Cation Group I includes cations of the alkali metals, i.e., cations of the elements of the first group (the main group elements) of the Mendeleev Periodic System. Also included in this group are the cations of ammonium and magnesium (see Sec. 21).

Cation Group II is made up of the cations of the alkaline earth metals, i.e., cations of the elements of the second group (the main group elements) of the Periodic System (magnesium, see above). They are characterized by the insolubility of their carbonates and the solubility of their sulphides in water.

Cation Group III is made up of the cations of the elements of the third group of the Periodic System and the transition[1] metals of the fourth period (in their lower valence) with the exception of copper. The cations of this group are characterized by the insolubility in water of the sulphides and hydroxides formed by them and the solubility of these

[1] Transition metals are characterized by the presence of incompletely occupied inner electron shells. Transition metals include, for instance, the following elements of the fourth period of the Mendeleev Periodic System: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

compounds in dilute acids. Group III cations form insoluble sulphides which are precipitated by ammonium sulphide.

Cation Group IV is made up of copper (an element of the fourth period) and the cations of metals of the fifth and sixth periods of the Periodic System. Exceptions are those metals whose sulphides exhibit acidic properties (arsenic, antimony, and tin). The Group IV sulphides are insoluble in water and in dilute acids and they are therefore precipitated by hydrogen sulphide from dilute hydrochloric acid solutions.

Cation Group V is made up of the cations whose sulphides are soluble in ammonium polysulphide. Included in this group are arsenic, tin and antimony cations. Group V cations, just as Group IV cations, form sulphides that are precipitated by hydrogen sulphide in an acidic solution. However, the Group V sulphides, in contrast to the Group IV sulphides, dissolve in ammonium polysulphide solution or alkaline solution of potassium or sodium sulphide.

The Table given below indicates to which analytical groups the cations considered in this textbook belong.

Analytical Classification of the Cations

Group	Group reagent	Cations
I	There is no group reagent	K^+, Na^+, NH_4^+, Mg^{2+}
II	$(NH_4)_2CO_3$	Ba^{2+}, Sr^{2+}, Ca^{2+}
III	$(NH_4)_2S$ or H_2S in the presence of NH_4OH	Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}
IV	H_2S in the presence of HCl	Ag^+, Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}
V	H_2S in the presence of HCl with subsequent dissolving of the precipitate in ammonium polysulphide or alkaline solution of K_2S or Na_2S	As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}

CHAPTER VII

Group I Cations

(K^+, Na^+, NH_4^+, Mg^{2+})

21. Group Characteristics

The first analytical group, as has already been stated, has no group reagent, i.e., a single precipitant that would precipitate all the cations of this group simultaneously. It is characteristic of this group that most of the salts formed by the cations in it (those of the alkali metals and ammonium) are soluble in water.

The NH_4^+ ion is included in Group I because the solubility of its salts resembles that of the salts of the alkali metals, especially those of potassium. Group II cations are separated from Group I cations by precipitation with ammonium carbonate, $(NH_4)_2CO_3$, in the presence of NH_4OH and NH_4Cl. Under these conditions, the magnesium ions remain in solution together with those of the alkali metals. Therefore, it is proper to include the magnesium ion in Group I rather than in Group II.

22. Reagents Used to Detect Group I Cations

1. Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, a complex salt that dissociates according to the equation

$$Na_3[Co(NO_2)_6] \rightleftarrows 3Na^+ + [Co(NO_2)_6]^{3-}$$

When an alkali acts on $Na_3[Co(NO_2)_6]$ solution, a brown precipitate of $Co(OH)_3$ is formed:

$$Na_3[Co(NO_2)_6] + 3NaOH = Co(OH)_3\downarrow + 6NaNO_2$$

Strong acids also decompose the complex ion:

$$2Na_3[Co(NO_2)_6] + 10HCl = 6NaCl + 2CoCl_2 + 5NO + \\ + 7NO_2 + 5H_2O$$

Acetic acid does not decompose $Na_3[Co(NO_2)_6]$, therefore, this reagent can be used in neutral or in acetic acid solutions.

Sodium cobaltinitrite is readily soluble in water, whereas $K_2Na[Co(NO_2)_6]$, $K_2Ag[Co(NO_2)_6]$, $K_3[Co(NO_2)_6]$, and the corresponding ammonium salts are insoluble in water.

2. Magnesium uranyl acetate, $Mg[(UO_2)_3(C_2H_3O_2)_8]$, and zinc uranyl acetate, $Zn[(UO_2)_3(C_2H_3O_2)_8]$. Uranyl is the term for the bivalent UO_2^{2+} cation. It combines with acid radicals to form uranyl salts, for example, uranyl acetate, $UO_2(CH_3COO)_2$. With salts of monobasic acids, for instance with acetates, uranyl salts form complex compounds. Examples of such compounds are the above-mentioned salts: zinc uranyl acetate and magnesium uranyl acetate. Sometimes two cations are outside the coordination sphere of the complex, for example, $KZn[(UO_2)_3(CH_3COO)_9]$ or $KMg[(UO_2)_3(CH_3COO)_9]$. These salts are readily soluble in water, whereas the similar sodium salts are only sparingly soluble. Therefore, zinc uranyl acetate and magnesium uranyl acetate are used as reagents for identifying Na^+ ions.

3. Potassium dihydrogen antimonate, KH_2SbO_4, is an acid salt of antimonic acid. The reagent can also be dihydrogen potassium pyroantimonate, $K_2H_2Sb_2O_7 \cdot H_2O$, or potassium antimonate, $K[Sb(OH)_6]$. The latter is obtained by the addition of water on dissolving KH_2SbO_4:

$$KH_2SbO_4 + 2H_2O = K[Sb(OH)_6]$$

The action of an acid on a KH_2SbO_4 solution produces an amorphous precipitate of meta-antimonic acid, $HSbO_3$:

$$KH_2SbO_4 + HCl = HSbO_3\downarrow + KCl + H_2O$$

$$H_2SbO_4^- + H^+ = HSbO_3\downarrow + H_2O$$

Therefore, KH_2SbO_4 can be used as a reagent only in a neutral or weak-alkaline solution. Sodium dihydrogen antimonate, NaH_2SbO_4, and magnesium dihydrogen antimonate, $Mg(H_2SbO_4)_2$, are insoluble in water. Consequently, in neutral or weak-alkaline solutions KH_2SbO_4 can be used as a reagent for identifying sodium ions if there are no magnesium ions in the solution.

4. Nessler's reagent, $K_2[HgI_4]$, in an alkaline solution. $K_2[HgI_4]$ is a complex salt that dissociates according to the equation

$$K_2[HgI_4] \rightarrow 2K^+ + [HgI_4]^{2-}$$

Nessler's reagent is used to identify ammonium ions (see Sec. 26, *P*2[1]).

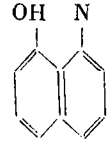
5. Sodium hydrogen phosphate, Na_2HPO_4 (dibasic sodium phosphate), which dissociates according to the equations

$$\text{first stage: } Na_2HPO_4 \rightleftarrows 2Na^+ + HPO_4^{2-}$$

$$\text{second stage: } HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$$

A Na_2HPO_4 solution contains Na^+, H^+, HPO_4^{2-}, and PO_4^{3-} ions. The concentration of these ions are not the same because Na_2HPO_4 dissociates completely, whereas HPO_4^{2-}, only negligibly. Consequently, the concentration of HPO_4^{2-} ions in a Na_2HPO_4 solution considerably exceeds that of PO_4^{3-} ions. When this salt reacts with ions whose phosphates are insoluble, acid or neutral salts may be precipitated. Neutral salts are precipitated when their solubility is considerably less than that of the acid salts. In the presence of alkalies, neutral salts (for the most part, double salts) are precipitated. For example, Na_2HPO_4 in the presence of NH_4OH forms $MgNH_4PO_4$ with magnesium salts.

6. 8-Hydroxyquinoline (oxyn)



The hydrogen in the hydroxyl group can be replaced by a metal to form hydroxyquinolinates. 8-Hydroxyquinoline is used as a reagent to identify Mg^{2+} ions.

23. Procedure and Reporting of Test Results

Before beginning the study of the cations of each group, copy the form of the Table for reporting the results of the reactions of the given group into the laboratory notebook and proceed to study the properties of the cations in the order given in the Table.

It is recommended that the results of tests for Group I cations be tabulated in the following form:

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[1] The designation *P* stands for procedure of analysis.

Reagents	Cations			
	K^+	Na^+	NH_4^+	Mg^{2+}
Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$ . .				
Magnesium uranyl acetate, $Mg\,[(UO_2)_3(C_2H_3O_2)_8]$, or				
Zinc uranyl acetate, $Zn\,[(UO_2)_3(C_2H_3O_2)_8]$				
Potassium dihydrogen antimonate, KH_2SbO_4				
Flame test				

Proceed to study the reactions of potassium and sodium ions.

1. First study the reaction of K^+ ions with sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$. Place 3-5 drops of KCl or KNO_3 solution in a test tube, add 2 or 3 drops of acetic acid and 3-5 drops of $Na_3[Co(NO_2)_6]$ solution. Note the colour of the precipitate and record it in the Table. Write the equation for the reaction in your laboratory notebook. Compare all your observations and recorded data with the reactions given in the textbook (see Sec. 24, *P*1).

2. Then study the two reactions of Na^+ ions: with magnesium uranyl acetate or zinc uranyl acetate and with potassium dihydrogen antimonate.

(a) To 3-5 drops of a solution of a sodium salt (NaCl or $NaNO_3$) add 3-5 drops of CH_3COOH and 5-8 drops of magnesium uranyl acetate or zinc uranyl acetate solution. Rub a glass rod against the walls of the test tube and observe the formation of a precipitate. Record your observations in the Table and write the equation for the reaction in your notebook.

(b) Place 5-8 drops of a sodium salt and the same amount of KH_2SbO_4 solution in a test tube and rub a glass rod against the walls of the test tube. Observe the formation of a heavy white crystalline precipitate of NaH_2SbO_4. Record the results in the Table and write the equation for the reaction in your notebook.

Shake up the liquid and precipitate and divide the mixture into three portions in separate test tubes. To the con-

tents of the first test tube add HCl solution and observe the formation of an amorphous precipitate of meta-antimonic acid, $HSbO_3$ (see Sec. 25, *P*2). To the contents of the second test tube add KOH solution. The precipitate will dissolve in a large quantity of alkali solution. Heat the contents of the third test tube; the precipitate of NaH_2SbO_4 is slightly soluble in hot water.

3. Flame tests. Clean a platinum or nichrome wire (see Sec. 24, *P*2), heat it strongly, immerse it into a test tube containing a potassium salt solution (or into solid potassium salt in the form of a powder), insert it into the nonluminous flame of a gas burner and note the colour of the flame. Repeat the same test immersing a clean wire into sodium salt solution (see Sec. 25, *P*3). Record the test results in the Table.

After that, carry out the tests for ammonium and magnesium ions, record the test results in the Table, and write the equations for the reactions in your laboratory notebook.

24. Tests for Potassium Ion, K^+

1. Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, in neutral or acetic acid solutions containing K^+ ions yields a yellow crystalline precipitate of sodium-potassium cobaltinitrite, $K_2Na[Co(NO_2)_6]$:

$$2KNO_3 + Na_3[Co(NO_2)_6] = K_2Na[Co(NO_2)_6]\downarrow + 2NaNO_3$$

$$2K^+ + 2NO_3^- + 3Na^+ + [Co(NO_2)_6]^{3-} =$$

$$= K_2Na[Co(NO_2)_6]\downarrow + 2Na^+ + 2NO_3^-$$

$$2K^+ + Na^+ + [Co(NO_2)_6]^{3-} = K_2Na[Co(NO_2)_6]\downarrow$$

NH_4^+ ions interfere with the detection of the presence of K^+ ions because they form with $Na_3[Co(NO_2)_6]$ a precipitate of a similar colour and character as that formed by potassium ions.

Sodium cobaltinitrite cannot be used as a reagent in alkaline or strongly acidic solutions because alkalies and strong acids decompose the complex $[Co(NO_2)_6]^{3-}$ ion (see Sec. 22, *P*1).

$Na_3[Co(NO_2)_6]$ is the most sensitive reagent for the detection of potassium ions. When using it, however, it is neces-

sary to observe the following conditions: the solution under test must be neutral or it may contain acetic acid; it must not contain NH_4^+ ions.

Procedure. Neutralize 3-5 drops of the solution under test that is free of NH_4^+ ions; if the solution is alkaline, add 2*N* acetic acid drop by drop until the solution is acidic to litmus; if the solution is acidic, add 2*N* NaOH dropwise until the solution is weak-alkaline and then add a few drops of acetic acid to make the solution acidic. To this solution, with a pH = 3-4 (determined by indicator paper), add 3-5 drops of $Na_3[Co(NO_2)_6]$ solution. The appearance of a yellow crystalline precipitate indicates the presence of K^+ ions. The reagent used is a freshly prepared solution containing 0.5 g of $Na_3[Co(NO_2)_6]$ in 3 ml of water.

2. Flame test. Potassium salts, especially potassium chloride or nitrate, impart a pale violet colour to the nonluminous flame of the gas burner. Even in the presence of traces of sodium compounds, the violet colour is masked by a yellow coloration. If, however, the flame is observed through blue cobalt glass, an indigo prism, or a solution of methyl-violet dye, only the violet rays of potassium are visible, whereas the yellow rays of sodium are completely absorbed.

Procedure. First clean a platinum or nichrome wire by dipping it into concentrated HCl solution poured onto a small watch glass. Then insert the wire into the burner flame. If a coloured flame is produced, continue to clean the wire in the acid until there is no coloration of the flame.

Dip the clean platinum or nichrome wire into the substance under test (in the form of a powder or solution) and insert it into the nonluminous burner flame. Observe the colour of the flame through two cobalt glass plates or an indigo prism. If the potassium ion is present, the flame assumes a pale violet colour.

25. Tests for Sodium Ion, Na^+

1. Zinc uranyl acetate, $Zn[(UO_2)_3(C_2H_3O_2)_8]$, in neutral or acetic acid solutions forms with sodium salts a greenish-yellow crystalline precipitate of $NaZn[(UO_2)_3(CH_3CO_2)_9] \times$

$\times 9H_2O$ that is clearly discernible on a black background.

$$Na^+ + Zn[(UO_2)_3(C_2H_3O_2)_8] + CH_3COO^- + 9H_2O =$$
$$= NaZn[(UO_2)_3(C_2H_3O_2)_9] \cdot 9H_2O$$

Magnesium uranyl acetate can be used instead of zinc uranyl acetate. K^+, Mg^{2+}, NH_4^+ ions and those of the alkaline earth metals do not interfere with this test.

Procedure. Place in a test tube 3 or 4 drops of the solution under test (either a neutral or acetic acid solution; an acidic solution is neutralized with ammonia solution the excess of which is neutralized with acetic acid) and add 8-10 drops of zinc uranyl acetate or magnesium uranyl acetate. Rub a glass rod against the walls of the test tube. If sodium is present a greenish-yellow precipitate is formed.

2. Potassium dihydrogen antimonate, KH_2SbO_4, forms with Na^+ ions a white crystalline precipitate of sodium dihydrogen antimonate, NaH_2SbO_4, when in neutral or weak-alkaline solution (at pH = 7.5-8):

$$NaCl + KH_2SbO_4 = NaH_2SbO_4\downarrow + KCl$$
$$Na^+ + Cl^- + K^+ + H_2SbO_4^- = NaH_2SbO_4\downarrow + K^+ + Cl^-$$
$$Na^+ + H_2SbO_4^- = NaH_2SbO_4\downarrow$$

The precipitate of NaH_2SbO_4 is soluble in hot water and, partially, in alkalies.

The KH_2SbO_4 reagent is prepared as described in Appendix 3B.

Acids decompose KH_2SbO_4 (see Sec. 22 *P* 3).

Ammonium salts act the same way as acids on KH_2SbO_4 because aqueous solutions of ammonium salts, due to hydrolysis, contain hydrogen ions:

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

and the pH of the solution is reduced to such an extent that the reagent is decomposed.

Magnesium salts interfere with the detection of the presence of Na^+ because they also form crystalline precipitates that can easily be mistaken for NaH_2SbO_4

Hence, the reagent KH_2SbO_4 can be used to detect sodium ions only if the following conditions are observed: no NH_4^+ or Mg^{2+} ions should be present in the solution; the solution

must be neutral or weak-alkaline and sufficiently concentrated; the test should be carried out in the cold.

Procedure. To 5-8 drops of a neutral or weak-alkaline solution (pH = 7.5-8) add 5-8 drops of KH_2SbO_4 solution. Rub a glass rod against the walls of the test tube. The presence of Na^+ ions is indicated by the appearance of a white crystalline precipitate. A flocky precipitate does not indicate the presence of Na^+ ions because it can be meta-antimonic acid that is precipitated if the solution is strongly acidic. NaH_2SbO_4 is a heavy crystalline precipitate. It readily settles at the bottom of the test tube and partly adheres to its walls.

3. Flame test. Sodium compounds impart a yellow colour to the nonluminous flame of the gas burner.

Procedure. Wet a platinum or nichrome wire with concentrated HCl solution and heat it in the nonluminous flame of the burner until the yellow coloration of the flame disappears. Dip the clean wire into the solution under test (or into the powder if the investigated substance is a solid) and insert it carefully into the nonluminous flame of the burner. A yellow colour that persists for several seconds indicates the presence of sodium ions in the solution.

26. Ammonium. Tests for Ammonium Ion, NH_4^+

Ammonium salts, in their solubility, resemble the corresponding alkali salts, especially potassium salts.

On ignition, ammonium salts decompose and evaporate in contrast to the salts of alkali metals.

NH_4^+ ions form precipitates with almost all the reagents that precipitate K^+ ions. It can be detected by the following identification tests:

1. The alkali hydroxides, NaOH and KOH, and the hydroxides of alkaline earth metals, $Ca(OH)_2$ and $Ba(OH)_2$, on heating them with ammonium salts, liberate ammonia:

$$NH_4Cl + KOH = NH_4OH + KCl$$

$$NH_4^+ + Cl^- + K^+ + OH^- = NH_4OH + K^+ + Cl^-$$

$$NH_4^+ + OH^- = NH_3\uparrow + H_2O$$

The presence of ammonia is detected by its odour or by red litmus paper turning blue, and also if a strip of filter paper moistened with mercurous nitrate turns black.

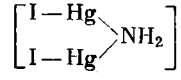
Procedure. To 3-5 drops of the solution under test or a grain of the solid product placed in a test tube add 4 or 5 drops of 2*N* alkali hydroxide solution. The reaction is carried out in an alkaline medium at a pH > 9. Cover the mouth of the test tube with moist red litmus paper or a strip of filter paper moistened with mercurous nitrate. The paper should not come in contact with the inner walls of the test tube. Heat the test tube carefully so that the liquid in it does not splash onto the paper. The presence of NH_4^+ ions is indicated if the litmus paper turns blue or the filter paper moistened with mercurous nitrate turns black.

2. Nessler's reagent, a mixture of solutions of the complex salt $K_2[HgI_4]$ and KOH forms with solutions of ammonium salts a red-brown precipitate of $NH_2Hg_2I_3$. If there are only traces of an ammonium salt present, no precipitate is formed but the solution assumes a yellow or brown colour.

$$NH_4Cl + KOH = NH_3 + KCl + H_2O$$

$$NH_3 + 2K_2[HgI_4] + KOH = NH_2Hg_2I_3\downarrow + 5KI + H_2O$$

The structural formula of $NH_2Hg_2I_3$ is



Procedure. Place 1 or 2 drops of the solution under test in a test tube, add 5-10 drops of water and 3 or 4 drops of Nessler's reagent. In the presence of NH_4^+ or NH_3 a red-brown precipitate appears or the solution assumes a yellow or brown colour.

27. Magnesium. Tests for Magnesium Ion, Mg^{2+}

Magnesium is bivalent in all its compounds. It forms only one oxide, MgO, with basic properties. The majority of magnesium salts are soluble in water. The insoluble magnesium compounds are: the hydroxide, phosphate, hydrogen phosphate, carbonate, oxalate, ferrocyanide, ferricyanide, fluoride, dihydrogen antimonate, and hydroxyquinolinate.

1. The alkali hydroxides, NaOH and KOH, and the hydroxides of alkaline earth metals, $Ca(OH)_2$ and $Ba(OH)_2$, yield with soluble magnesium salts a white gelatinous precipitate

of magnesium hydroxide, $Mg(OH)_2$:

$$Mg^{2+} + 2OH^- = Mg(OH)_2\downarrow$$

Magnesium hydroxide is not precipitated in the presence of a large quantity of an ammonium salt. Magnesium hydroxide is soluble in acids:

$$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$$

Procedure. To 2 or 3 drops of a solution of a magnesium salt add 3 or 4 drops of 2*N* NaOH or KOH solution. A white amorphous precipitate appears that dissolves on being treated with an acid.

2. **Aqueous ammonia solution** forms with Mg^{2+} ions a small precipitate of $Mg(OH)_2$. Precipitation is incomplete because the reaction is reversible:

$$MgCl_2 + 2NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl$$

Procedure. To 3-5 drops of a solution of a magnesium salt add 3-5 drops of 2*N* NH_4OH solution. A small precipitate is formed.

3. **Aqueous ammonia solution** in the presence of ammonium salts does not form a precipitate with Mg^{2+} ions because ammonium salts decrease the dissociation of NH_4OH and the concentration of hydroxyl ions becomes less than that necessary for a saturated $Mg(OH)_2$ solution.

Procedure. To 2 or 3 drops of a solution of a magnesium salt add 3-5 drops of 2*N* NH_4Cl solution and 2 or 3 drops of 2*N* NH_4OH solution. No precipitate appears.

4. **Sodium hydrogen phosphate, Na_2HPO_4,** in the presence of NH_4OH and NH_4Cl[1] forms with Mg^{2+} ions a white crystalline precipitate of the double salt magnesium ammonium phosphate, $MgNH_4PO_4$:

$$MgCl_2 + NH_4OH + Na_2HPO_4 = MgNH_4PO_4\downarrow + H_2O + 2NaCl$$

$$Mg^{2+} + 2Cl^- + NH_4OH + 2Na^+ + HPO_4^{2-} =$$

$$= MgNH_4PO_4\downarrow + H_2O + 2Na^+ + 2Cl^-$$

$$Mg^{2+} + NH_4OH + HPO_4^{2-} = MgNH_4PO_4\downarrow + H_2O$$

Magnesium ammonium phosphate is readily soluble in acids and practically insoluble in 2.5 per cent ammonia solution.

[1] Ammonium chloride, NH_4Cl, is added to prevent precipitation of $Mg(OH)_2$.

Procedure. Place 3-5 drops of the solution under test in a test tube and add to it 2 or 3 drops of 2*N* NH_4Cl solution, 2 or 3 drops of 2*N* HCl solution, and 3 or 4 drops of Na_2HPO_4 solution. No precipitate should appear. If a precipitate is formed, add 2*N* HCl solution drop by drop until it is dissolved. To the clear solution add a drop of phenolphthalein indicator and 2*N* ammonia solution a drop at a time, carefully shaking up the contents of the test tube after the addition of each successive drop. Add the ammonia solution until the indicator turns a pink colour that does not disappear. In the presence of magnesium ions, a crystalline precipitate is formed. From dilute solutions the precipitate forms very slowly. Precipitation can be accelerated by cooling the solution and rubbing a glass rod against the walls of the test tube.

5. **8-Hydroxyquinoline, C_9H_6NOH**[1], in an ammoniacal solution (pH = 9.5-12) forms with Mg^{2+} ions a yellow acicular crystalline precipitate of $Mg(C_9H_6NO)_2$ that is soluble in mineral acids. The cations of alkali and alkaline earth metals do not interfere with this test for Mg^{2+} ions, but Group III cations do.

Procedure. To 3-5 drops of the solution under test add 1 or 2 drops of phenolphthalein solution and 2*N* NH_3 solution drop by drop until a pink colour appears. Heat the mixture to boiling and add, dropwise, a 3 per cent ammonia solution of hydroxyquinoline. In the presence of magnesium, a yellow crystalline precipitate is formed.

Questions and Exercises

1. What reagent is used for detecting the K^+ ion?
2. Write the equation for the reaction between potassium phosphate and sodium cobaltinitrite.
3. Why is it impossible to detect K^+ ions with the $Na_3[Co(NO_2)_6]$ reagent in alkaline or strongly acidic solutions?

Write the equations for the reactions of an alkali hydroxide and strong acid with $Na_3[Co(NO_2)_6]$.

4. Why is it necessary to free the solution from NH_4^+ ions prior to determining K^+ ions?
5. What are the tests for identifying the Na^+ ion?

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[1] See Appendix 3B for a description of the preparation of this reagent.

6. Why can the Na^+ ion be detected by the KH_2SbO_4 reagent only in a neutral or weak-alkaline solution?

7. What are the tests for identifying NH_4^+ and Mg^{2+} ions? Write the equations for the reactions that occur in them.

8. Why is NH_4OH added to the solution under test when determining Mg^{2+} ions with the sodium hydrogen phosphate reagent?

28. Analysis of Mixture of Group I Cations

Before proceeding to make the tests for Group I cations, it is necessary to ascertain whether the mixture contains NH_4^+ ion which interferes with the detection of K^+ ion and also of Na^+ ion (if the latter is detected with KH_2SbO_4 reagent).

If there are ammonium ions in the solution under test, the ammonium salts present must be removed by ignition (taking advantage of their volatility). After that, tests are conducted to detect K^+, Mg^{2+}, and Na^+ ions.

Analysis of Group I cations should be carried out in the following sequence:

1. Test for ammonium ion. The ammonium ion can be detected by means of an alkali hydroxide or Nessler's reagent. To detect NH_4^+ ion with an alkali hydroxide, add 8-10 drops of 2*N* alkali hydroxide solution to 3-5 drops of the solution under test in a test tube. Cover the test tube with moist red litmus paper and heat carefully to the boiling point, taking care that no alkali splashes onto the paper and that the paper does not come in contact with the inner walls of the test tube. If the paper turns blue, the presence of NH_4^+ ions is indicated. For detecting NH_4^+ ions with Nessler's reagent, add 3-5 drops of this reagent to 2 or 3 drops of the solution under test. In the presence of NH_4^+ ions, a red-brown precipitate appears or the solution assumes a yellow or brown colour.

2. Removal of ammonium salts. If NH_4^+ ions are present, it is necessary to remove them because, as has been previously noted, they interfere with the detection of K^+ ions. For this purpose transfer 3-5 ml of the solution under test to a small evaporating dish, put it in a water bath, and evaporate the solution to dryness. If a crust forms on the surface of the liquid, dissolve it by stirring the solution with a glass rod. Place the evaporating dish with the residue

under a hood on a small sand bath or clay triangle and ignite over an open flame, at first a weak flame and then a stronger one, until white fumes are no longer evolved. Stir the contents of the dish from time to time to avoid spattering. To remove the ammonium salts more effectively, heat the dish strongly, holding the burner in the hand and directing the flame on the walls and bottom of the dish.

After all the NH_3 has been evolved, cool the dish, crush the dry residue with the end of a glass rod, then wet it with a few drops of concentrated HNO_3. Evaporate the solution to dryness and ignite the residue once more.

Ammonium salts must be completely removed since even traces will interfere with the detection of potassium ions. To ascertain whether the ammonium salts have been completely removed, add a particle of the dry residue to 3-5 drops of Nessler's reagent. The absence of a red-brown precipitate or yellow or brown coloration of the solution indicates completeness of removal of ammonium salts. In case of incomplete removal of ammonium salts, continue to ignite the dry residue. Only after making sure that ammonium salts are completely removed, cool the dish, add 1-2 ml of distilled water and 3-5 drops of 2*N* acetic acid solution[1]. Centrifuge the solution and test for K^+, Mg^{2+}, and Na^+ ions in the supernatant.

3. Flame test (preliminary test). Wet a freshly cleaned platinum or nichrome wire in the solution obtained (supernatant) and insert it into the nonluminous flame of the gas burner. An intense yellow colour that persists 20-30 seconds indicates the presence of the sodium ion, whereas a violet colour visible through cobalt glass or an indigo solution indicates the presence of the potassium ion. This test, however, is only tentative.

4. Test for potassium ion. After removing ammonium salts (*P* 2) transfer 3-5 drops of the solution to a test tube and add 1 or 2 drops of phenolphthalein solution. If on doing so the solution is colourless (acidic or neutral), add 2*N* NaOH solution drop by drop till the indicator turns pink (alkaline reaction); then add 2*N* CH_3COOH solution

[1] Acetic acid is added to dissolve any basic magnesium salts that may be present.

a drop at a time until the solution becomes colourless (pH = 3-4). To the resulting acetic acid solution add 3-5 drops of $Na_3[Co(NO_2)_6]$. The appearance of a yellow precipitate indicates the presence of the potassium ion.

5. Tests for magnesium ion:

(a) to 3-5 drops of the solution obtained after removal of ammonium salts (see *P* 2) or to 3-5 drops of the solution under test add 1 ml of 2*N* HCl solution, 2 or 3 drops of NH_4Cl solution, 3 or 4 drops of Na_2HPO_4 solution and a drop of phenolphthalein indicator. No precipitate should appear. If one does appear, add a few drops of 2*N* HCl solution. Add to the resulting clear solution 2*N* ammonia solution drop by drop until the indicator assumes a persistent pink colour. The appearance of a white crystalline precipitate indicates the presence of Mg^{2+} ions.

(b) to 3-5 drops of the solution under test or the solution obtained after removing NH_4^+ salts (see *P* 2) add, in the presence of phenolphthalein, 3 or 4 drops of 4*N* NH_4OH solution till a persistent pink colour appears and then 3-5 drops of hydroxyquinoline solution. The formation of a greenish yellow precipitate indicates the presence of magnesium ions.

6. Test for sodium ions with zinc uranyl acetate or magnesium uranyl acetate. To 3-5 drops of the solution under test or the solution freed from ammonium salts (see *P* 2) add 8-10 drops of either $Zn[(UO_2)_3(C_2H_3O_2)_8]$ or $Mg[(UO_2)_3(C_2H_3O_2)_8]$. Shake the mixture and rub a glass rod against the walls of the test tube. The appearance of a yellowish-green precipitate indicates the presence of Na^+ ions.

7. Test for sodium ions with potassium dihydrogen antimonate reagent. This reagent must be used in the absence of NH_4^+ and Mg^{2+} ions, in a neutral or weak-alkaline solution. To remove Mg^{2+} ions, to the solution obtained after freeing the solution under test from ammonium salts (see *P* 2) add 2*N* aqueous KOH until the solution is strongly alkaline to litmus or indicator paper. Heat the mixture to boiling and centrifuge. To the supernatant obtained after removing Mg^{2+} ions, add HCl to neutralize the excess KOH until the solution is weak-alkaline. Evaporate the solution to a small volume (not more than 1 ml) and deter-

mine the reaction of the solution with the aid of litmus paper. If the solution is acidic or neutral, add a few drops of 2*N* KOH solution. To the weak-alkaline solution (pH = = 7.5-8) obtained add an equal volume of KH_2SbO_4. Rub a glass rod against the walls of the test tube. The presence of Na^+ ions is indicated by the appearance of a white crye stalline precipitate.

CHAPTER VIII

Solubility Product

29. Solubility-Product Principle

A system consisting of a saturated solution in contact with the residual solid is a heterogeneous (two-phase) system, whereas a true solution is a homogeneous (one-phase) system.

Heterogeneous systems are of great significance in analytical chemistry. They are encountered in the process of precipitation and the separation and washing of precipitates.

When a solid electrolyte is dissolved in water, the ions are hydrated to produce hydrates which are unstable combinations of the ions with molecules of water. These hydrated ions break away from the surface of crystals and pass into aqueous solution. At the same time a reverse process, crystallization, takes place (i.e., precipitation of ions from the solution onto the surface of the crystals). When the rate of solution and rate of precipitation become equal, the solution becomes saturated and two cases of dynamic equilibrium come to exist:

(1) between the solid substance (precipitate) and its unionized molecules:

$$\underset{\text{solid phase}}{AB} \rightleftarrows \underset{\text{solution}}{AB}$$

(2) in the solution itself between the unionized molecules of the dissolved electrolyte and its ions:

$$\underset{\text{solution}}{AB} \rightleftarrows A^+ + B^-$$

The general state of equilibrium of such a system can be presented by the following schematic equation:

$$\underset{\text{precipitate}}{AB} \rightleftarrows \underset{\text{solution}}{AB \rightleftarrows A^+ + B^-}$$

For example, for a saturated solution of silver acetate in the presence of the solid salt the schematic equation is

$$\underset{\text{solid phase}}{CH_3COOAg} \rightleftarrows \underset{\text{solution}}{CH_3COOAg \rightleftarrows Ag^+ + CH_3COO^-}$$

The concentration of the dissolved substance in a saturated solution varies with the temperature. In other words, at a given temperature such a solution contains a definite amount of dissolved molecules of the substance. Hence, in a saturated solution of an electrolyte the concentration of undissociated molecules of this electrolyte is a constant value at a given temperature. An attempt to increase the concentration of the dissolved substance in a saturated solution results in the instantaneous appearance of a precipitate. This can be illustrated by the following experiment. Dissolve 1-2 g of silver acetate in 100 ml of water by heating the mixture. On cooling the solution, excess silver acetate is precipitated in the form of white flakes. Separate the precipitate from the solution by filtering or centrifuging. Pour equal portions of the clear solution into three separate flasks. To one of them add 10 ml of 20 per cent $AgNO_3$ solution; to another, 10 ml of 20 per cent CH_3COONa solution; and to the third, 10 ml of 20 per cent $NaNO_3$ solution. A precipitate will appear in the first two flasks, whereas there will be no precipitate in the third flask. How can this be explained? No chemical action takes place in the flasks between the substances. However, the addition of an electrolyte with a common ion increases the concentration in the solution of Ag^+ ions in the first case, and CH_3COO^- ions in the second case. This in turn increases the concentration of undissociated CH_3COOAg molecules. Since the concentration of the latter in a saturated solution is a constant value, the newly formed CH_3COOAg molecules are precipitated. This conclusion is also confirmed by the fact that no precipitate is formed in the flask to which

$NaNO_3$ solution, i.e., an electrolyte that does not contain ions in common with CH_3COOAg, was added.

If in this experiment the volume of the solution is increased (i.e., water is added) after the precipitate is formed, the latter will be dissolved. This proves that the precipitate was previously formed because the number of undissociated molecules present was greater than could be dissolved in the original volume of the solvent.

Hence, it follows that the addition to a solution of a salt of an electrolyte with a common ion decreases the solubility of the salt.

Let us consider the solution of a sparingly soluble electrolyte, for example, AgCl.

It dissociates as follows:

$$AgCl \rightarrow Ag^+ + Cl^-$$

The dissociation constant equals

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

The concentration of undissociated molecules in a saturated solution is a constant value. Hence,

$$[Ag^+][Cl^-] = K[AgCl] = \text{Constant}$$

This means that $[Ag^+][Cl^-]$ is also a constant value.

Thus, *in a saturated solution of a slightly soluble electrolyte the product of the ion concentrations is a constant at a given temperature.* The constant referred to is called the solubility product and is denoted as S_{MeA} where MeA is the formula of the given electrolyte. For example,

$$S_{AgCl} = [Ag^+][Cl^-]$$

The expressions for the solubility product of other sparingly soluble compounds are:

$$S_{AgI} = [Ag^+][I^-]$$

$$S_{Ag_2S} = [Ag^+]^2[S^{2-}]$$

$$S_{MgNH_4PO_4} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$$

$$S_{Pb_3(PO_4)_2} = [Pb^{2+}]^3\,[PO_4^{3-}]^2$$

For an electrolyte with the formula Me_mA_n the solubility product is

$$S_{Me_mA_n} = [Me^{n+}]^m[A^{m-}]^n$$

Thus, *the concentration of each ion in the equation for the solubility product is raised to the power equal to the number of these ions in the given molecule.* In a saturated solution the product of the concentrations of the constituent ions of a precipitate is a constant and does not depend on the presence of other electrolytes with other ions in the solution.

A solution is said to be saturated when the product of the concentrations of the ions in the solution is equal to the solubility product.

Hence, for the electrolyte MeA, the solution is unsaturated if the product of the concentrations in the solution is less than the solubility product, i.e., $[M^+]\,[A^-] < S_{MeA}$; the solution is saturated if the product of the concentrations of the ions in the solution is equal to the solubility product, i.e., $[Me^+][A^-] = S_{MeA}$ (in this case no precipitate is formed); and a precipitate is formed in a solution if the product of the concentrations of the ions in the solution is greater than the solubility product, i.e., $[Me^+][A^-] > S_{MeA}$.

The rule for the solubility product is: *a precipitate is formed when the product of the ion concentrations in the solution is greater than the value of the solubility product.* The concentration of one of the ions may be greater than the concentration of the other ion.

Experiments have shown that this rule does not apply to electrolytes that dissolve readily. It applies only to electrolytes with a solubility in water that is not greater than 0.01 mole per litre.

The numerical values of the solubility products of various sparingly soluble electrolytes are given in Appendix 6.

30. Calculation of Solubility Product and Solubility

The solubility product of a slightly soluble electrolyte can be calculated if its solubility is known, and vice versa, the molar solubility of such an electrolyte in water or in

a solution containing a common ion can be calculated if the solubility product of this electrolyte is given.

(a) **Calculation of the solubility product of an electrolyte from its solubility.** The solubility product is found as follows:

(1) write the equation for the dissociation of the electrolyte the solubility product of which must be calculated;

(2) express the solubility product of the electrolyte as the product of the concentrations of its ions;

(3) calculate the molar solubility of the substance, i.e., the solubility in moles per litre;

(4) calculate the concentration of each ion at equilibrium, using the dissociation equation and the molar solubility found above;

(5) substitute the values for the concentrations of the ions found in (4) in the expression for the solubility product obtained in (2) and make the necessary calculations.

Example 1. Calculate the solubility product of $MgCO_3$ if 1 litre of its saturated solution contains 0.533 g of $MgCO_3$ at 20°C.

Solution. 1. The dissociation equation is

$$MgCO_3 \rightleftarrows Mg^{2+} + CO_3^{2-} \qquad (1)$$

2. The expression for the solubility product is

$$S_{MgCO_3} \rightleftarrows [Mg^{2+}][CO_3^{2-}] \qquad (2)$$

3. Calculate the molar solubility of $MgCO_3$, i.e., the number of moles of the salt dissolved in 1 litre of solution (see Sec. 2).

Since the molecular weight of $MgCO_3$ equals 84.32 g, the molar solubility of $MgCO_3$ will be

$$\frac{0.533}{84.32} = 0.00632 = 6.32 \cdot 10^{-3} \text{ mole/lit}$$

4. Calculate the concentration of the Mg^{2+} and CO_3^{2-} ions at equilibrium.

Each mole of $MgCO_3$, on dissociating, forms 1 gram-ion of Mg^{2+} and 1 gram-ion of CO_3^{2-} as seen from equation (1). Hence, the Mg^{2+} and CO_3^{2-} ions in the solution have the same concentration equal to the molar solubility of the salt:

$$[Mg^{2+}] = 6.32 \cdot 10^{-3} \text{ g-ion/lit}; \quad [CO_3^{2-}] = 6.32 \cdot 10^{-3} \text{ g-ion/lit}$$

5. Substitute the values of the concentrations of the Mg^{2+} and CO_3^{2-} ions in the expression for the solubility product given by equation (2):

$$S_{MgCO_3} = [Mg^{2+}][CO_3^{2-}] = 6.32 \cdot 10^{-3} \times 6.32 \cdot 10^{-3} = 4.0 \cdot 10^{-5}$$

Thus, the solubility product of $MgCO_3$ is equal to $4.0 \cdot 10^{-5}$.

(b) **Calculation of the solubility of an electrolyte in pure water, from its solubility product.** The solubility is found as follows:

(1) write the equation for the dissociation of the substance the solubility of which must be calculated;

(2) express the solubility product of the substance as the product of the concentrations of its ions;

(3) denote the molar solubility of the substance as x mole/lit;

(4) calculate the concentration of each ion at equilibrium, using the dissociation equation of the substance;

(5) substitute the values for the concentrations of the ions found in (4) in the expression for the solubility product obtained in (2) and make the necessary calculations.

Example 2. Calculate the solubility of AgCl in milligrams per litre if it is known that S_{AgCl} equals $1.78 \cdot 10^{-10}$.

Solution. 1. The dissociation equation is

$$AgCl \rightleftarrows Ag^+ + Cl^- \qquad (1)$$

The concentration of Ag^+ ions is equal to the concentration of Cl^- ions, i.e.,

$$[Ag^+] = [Cl^-]$$

2. The solubility product is

$$S_{AgCl} = [Ag^+][Cl^-] \qquad (2)$$

3. Denote the molar solubility of AgCl as x mole/lit. Since complete dissociation of the dissolved salt occurs in the solution, the concentration of each ion is equal to the concentration of the salt, i.e., its molar solubility:

$$[Ag^+] = x \qquad \text{and} \qquad [Cl^-] = x$$

4. Substitute these values in the expression for the solubility product given in equation (2):

$$S_{AgCl} = x \cdot x$$

Since it has been stated that the solubility product $S_{AgCl} = 1.78 \cdot 10^{-10}$, we can write $1.78 \cdot 10^{-10} = x^2$.

5. Solve the equation obtained and calculate the molar solubility and solubility of AgCl in milligrams per litre.

$$1.78 \cdot 10^{-10} = x^2; \qquad x = \sqrt{1.78 \cdot 10^{-10}} = 1.33 \cdot 10^{-5} \text{ mole/lit}$$

Thus, $1.33 \cdot 10^{-5}$ moles are dissolved in 1 litre of a saturated solution. Since the molecular mass of AgCl is equal to 143.34, the solubility of AgCl equals

$$143.34 \times 1.33 \cdot 10^{-5} = 191 \cdot 10^{-5} = 1.91 \cdot 10^{-3} \text{ g/lit} = 1.91 \text{ mg/lit}$$

Example 3. Calculate the solubility of $Mg(OH)_2$ in milligrams per litre if $S_{Mg(OH)_2}$ is equal to $6.0 \cdot 10^{-10}$.

Solution. 1. The dissociation equation is

$$Mg(OH)_2 \rightleftarrows Mg^{2+} + 2OH^- \qquad (1)$$

2. The expression for the solubility product is

$$S_{Mg(OH)_2} = [Mg^{2+}][OH^-]^2 \qquad (2)$$

3. Denote the molar solubility of $Mg(OH)_2$ as x mole/lit, then we can write $[Mg^{2+}] = x$ and $[OH^-] = 2x$ in accordance with equation (1).

4. Substitute x and $2x$ in the expression for the solubility product given by equation (2):

$$S_{Mg(OH)_2} = x\,(2x)^2 = 4x^3$$

Hence,

$$4x^3 = 6.0 \cdot 10^{-10}$$

$$x^3 = 1.5 \cdot 10^{-10}$$

$$x = \sqrt[3]{1.5 \cdot 10^{-10}} = \sqrt[3]{150 \cdot 10^{-12}} = 5.31 \cdot 10^{-4}$$

Thus, the solubility of $Mg(OH)_2$ is equal to $5.31 \times \times 10^{-4}$ mole/lit. Since the molecular mass of $Mg(OH)_2$ is 58.33, the solubility of $Mg(OH)_2$ equals

$$58.33 \times 5.31 \cdot 10^{-4} = 310 \cdot 10^{-4} = 31.0 \cdot 10^{-3} \text{ g/lit} = 31.0 \text{ mg/lit}$$

31. Common-Ion Effect

In a saturated solution of a slightly soluble electrolyte, an increase in the concentration of the ions results in the formation of a precipitate. This can be illustrated by the following experiment.

Dissolve 12-15 g of potassium chlorate, $KClO_3$, in 200 ml of hot water. On cooling the resulting solution, excess $KClO_3$ is precipitated from the solution. Filter the precipitate and pour equal portions of the clear solution into three flasks. To one of them add 5 ml of 20 per cent K_2SO_4 solution; to another, 5 ml of 20 per cent $NaClO_3$ solution; to the third flask, 5 ml of 20 per cent NaCl solution. The solutions in the first and second flasks become turbid in a minute, whereas the solution in the third flask remains clear.

How can this be explained? No reactions took place in the flasks. However, on adding an electrolyte with a common ion, the concentration of K^+ ions, in the first case, and ClO_3^- ions, in the second case, was increased in the solution. That is the reason why in both cases $KClO_3$ was precipitated. Hence, precipitation occurs only because K^+ and ClO_3^- ions are present in the given solution in a quantity that is greater than that in the saturated solution. The solution remains clear in the third flask to which NaCl was added because no common ion was introduced into the solution.

Therefore we can conclude that on adding a strong electrolyte having one of the ions contained in the dissolved substance, the solubility of the latter is decreased.

32. Effect of Other Conditions Upon Solubility of Precipitate

Effect of hydrogen ion concentration. The action of an acid on sparingly soluble salts of strong acids (for example, AgCl, $BaSO_4$) is the same as that of other electrolytes that have no ions in common with them, i.e., the solubility of the salt is somewhat increased due to the *salt effect.*

Sparingly soluble salts of weak acids are readily soluble in stronger acids. This can be explained by the fact that saturated solutions of such salts contain anions of a weak acid, that combine with the hydrogen ions of the added strong acid to form a slightly dissociated weak acid. For instance, due to the action of hydrogen ions on a $BaCO_3$ precipitate, the equilibrium between the precipitate and the ions

$$BaCO_3 \rightleftarrows Ba^{2+} + CO_3^{2-}$$

is shifted to the right as the carbonate ions combine with the hydrogen ions:

$$2H^+ + CO_3^{2-} = H_2CO_3$$

The carbonic acid formed decomposes, liberating CO_2. Hence, the concentration of CO_3^{2-} ions is decreased.

The effect of the acid on the dissolving of the precipitate depends on the solubility product of the given salt and on the dissociation constant of the weak acid produced. The greater the solubility product and the smaller the dissociation constant of the weak acid, the greater the effect of the added acid on the solubility of the precipitate. For example, all carbonates are soluble in weak acids; most of the phosphates are soluble in strong acids.

Effect of temperature. If dissolving of a substance in water is accompanied by absorption of heat, its solubility increases with rising temperature. Most of the precipitates met with in analytical chemistry belong to this type, i.e., they are more soluble in hot solutions than in cold ones. The solubility of some precipitates increases considerably; others, insignificantly. Thus, the solubility of lead chloride equals 10.9 g/lit at room temperature and 33.38 g/lit at 100°C, whereas the solubility of barium sulphate is 0.003 g/lit at 25°C and 0.004 g/lit at 100°C.

Effect of solvent. On adding an organic solvent to water, the solubility of inorganic salts usually decreases because polar compounds are more soluble in polar solvents than in nonpolar solvents. For example, 2.7 g of potassium perchlorate dissolve in 100 ml of water at 20°C, but only 0.0094 g in 100 ml of 97 per cent alcohol and 0.00364 g in 100 ml of normal butyl alcohol.

Problems

1. Calculate the solubility product of calcium carbonate if 0.69 mg of $CaCO_3$ is dissolved in 100 g of water at 20°C.

Ans. $4.8 \cdot 10^{-9}$

2. Calculate the solubility of silver bromide in milligrams per litre if $S_{AgBr} = 5.3 \cdot 10^{-13}$.

Ans. 0.13 mg/lit

3. Calculate the solubility of Ag_2CrO_4 in milligrams per litre if $S_{Ag_2CrO_4} = 1.1 \cdot 10^{-12}$.

Ans. 20 mg/lit

CHAPTER IX

Group II Cations

(Ba^{2+}, Sr^{2+}, Ca^{2+})

33. Group Characteristics

The second analytical group of cations includes the alkaline earth metals, barium, strontium, and calcium. It is characteristic of this group that their carbonates are not soluble in water, but are soluble in strong acids (HCl, HNO_3) and weak acids (CH_3COOH). The Group II sulphides (BaS, SrS, and CaS) are readily soluble in water. This distinguishes them from the cations of Groups III, IV, and V whose sulphides are insoluble in water. The Group II hydroxides ($Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$) are strong alkalies. The chromates ($BaCrO_4$, $SrCrO_4$, and $CaCrO_4$) differ from each other in their solubility (see Sec. 35, *P* 2). The sulphates ($BaSO_4$, $SrSO_4$, and $CaSO_4$) are sparingly soluble in water as well as in strong and weak acids; the most soluble of these salts is $CaSO_4$ (0.2 g in 100 g of water at 20°C). The oxalates (BaC_2O_4, SrC_2O_4, and CaC_2O_4) do not dissolve in water or in cold acetic acid, but dissolve in strong acids; calcium oxalate is the least soluble of these salts. The phosphates ($Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, and $Ca_3(PO_4)_2$) and the hydrogen phosphates ($BaHPO_4$, $SrHPO_4$, and $CaHPO_4$) are insoluble in water but they are soluble in acetic acid and in strong acids.

The chlorides, nitrates, acetates, bicarbonates, sulphides, and hydrosulphides, for example $BaCl_2$, $Ba(NO_3)_2$, $Ba(CH_3COO)_2$, $Ba(HCO_3)_2$, BaS, and $Ba(HS)_2$, are readily soluble in water.

Ba^{2+}, Sr^{2+}, and Ca^{2+} cations are colourless. Volatile compounds of these cations (for example, chlorides or nitrates) impart characteristic colours to the flame of a gas burner (see Sec. 35, *P* 9).

34. Reagents Used to Detect Group II Cations

1. Ammonium carbonate, $(NH_4)_2CO_3$. This is the group reagent for the second analytical group of cations.

Carbonic acid is dibasic and forms two series of salts: neutral salts, carbonates; and acid salts, bicarbonates (or

hydrocarbonates). Examples are: ammonium carbonate, $(NH_4)_2CO_3$, and ammonium bicarbonate, NH_4HCO_3. Barium, strontium, and calcium carbonates are insoluble in water, but the bicarbonates $Ba(HCO_3)_2$, $Sr(HCO_3)_2$, and $Ca(HCO_3)_2$ are readily soluble.

2. Potassium chromate, K_2CrO_4, and potassium dichromate, $K_2Cr_2O_7$. An aqueous solution of potassium chromate, K_2CrO_4, contains colourless K^+ ions and yellow chromate ions:

$$K_2CrO_4 \rightleftarrows 2K^+ + CrO_4^{2-}$$

An aqueous solution of potassium dichromate, $K_2Cr_2O_7$, contains colourless K^+ ions and orange-red $Cr_2O_7^{2-}$ ions:

$$K_2Cr_2O_7 \rightleftarrows 2K^+ + Cr_2O_7^{2-}$$

If an acid is added to a K_2CrO_4 solution, its colour changes from yellow to orange-red due to the formation of $K_2Cr_2O_7$:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O$$

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$$

On adding an alkali to a $K_2Cr_2O_7$ solution, it turns from orange-red to yellow as a result of the formation of K_2CrO_4:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

$$Cr_2O_7^{2-} + 2OH = 2CrO_4^{2-} + H_2O$$

Hence, an acid solution contains $Cr_2O_7^{2-}$ ions; an alkaline solution, CrO_4^{2-} ions.

3. Saturated solution of gypsum, $CaSO_4 \cdot 2H_2O$.

4. Ammonium oxalate, $(NH_4)_2C_2O_4$, is a salt of oxalic acid, $H_2C_2O_4$, which is dibasic and dissociates in two stages:

$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^-$$

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2-}$$

Barium, strontium, and calcium oxalates are insoluble in water.

5. Sodium rhodizonate, $Na_2C_6O_6$, is a water-soluble salt of rhodizonic acid. It consists of needle-like crystals violet in colour. The reagent used in this test is an aqueous solution containing 0.1 g of sodium rhodizonate in 100 ml of water. It gives coloured precipitates with Ba^{2+} and Sr^{2+}

35. Reactions of Group II Cations

(Barium, Strontium, and Calcium Ions)

The test results obtained on carrying out the reactions of Group II cations should be tabulated in the following form:

Reagent	Cations		
	Ba^{2+}	Sr^{2+}	Ca^{2+}
Ammonium carbonate, $(NH_4)_2CO_3$; action of acetic acid on precipitate formed on adding $(NH_4)_2CO_3$			
Potassium chromate, K_2CrO_4; action of HCl and CH_3COOH on precipitate formed on adding K_2CrO_4			
Potassium dichromate, $K_2Cr_2O_7$, plus sodium acetate, CH_3COONa			
Sulphuric acid, H_2SO_4			
Ammonium sulphate, $(NH_4)_2SO_4$			
Saturated solution of gypsum, $CaSO_4 \cdot 2H_2O$			
Ammonium oxalate, $(NH_4)_2C_2O_4$			
Sodium rhodizonate, $Na_2C_6O_6$			
Flame test			

In order to carry out each of the above-enumerated tests, take three test tubes: in one of them place 3-5 drops of a barium salt that is readily soluble in water; in another, a strontium salt; in the third, a calcium salt. To the contents of each test tube add one of the reagents listed in the Table.

1. Ammonium carbonate, $(NH_4)_2CO_3$, forms with Ba^{2+}, Sr^{2+}, and Ca^{2+} ions white amorphous precipitates of the carbonates, $BaCO_3$, $SrCO_3$, and $CaCO_3$, which on heating are converted to crystalline precipitates. The equations for the precipitation of barium carbonate are:

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3\downarrow + 2NH_4Cl$$

$$Ba^{2+} + 2Cl^- + 2NH_4^+ + CO_3^{2-} = BaCO_3\downarrow + 2NH_4^+ + 2Cl^-$$

$$Ba^{2+} + CO_3^{2-} = BaCO_3\downarrow$$

Sr^{2+} and Ca^{2+} ions give similar reactions.

The carbonates are salts of the very weak carbonic acid which is weaker than acetic acid. Therefore, they dissolve in strong acids (except H_2SO_4) and in acetic acid:

$$BaCO_3 + 2HCl = BaCl_2 + H_2CO_3;\ H_2CO_3 = H_2O + CO_2\uparrow$$

$$BaCO_3 + 2H^+ = Ba^{2+} + H_2CO_3 = Ba^{2+} + H_2O + CO_2\uparrow$$

$$BaCO_3 + 2CH_3COOH = Ba(CH_3COO)_2 + H_2O + CO_2\uparrow$$

$$BaCO_3 + 2CH_3COOH = Ba^{2+} + 2CH_3COO^- + H_2O + CO_2\uparrow$$

Similar reactions take place on dissolving strontium and calcium carbonates in acids.

Procedure. Place 5-6 drops of barium chloride or barium nitrate in a test tube; the same amount of strontium chloride or strontium nitrate in a second test tube; and calcium chloride or calcium nitrate in a third one. To each test tube add 3-5 drops of 2*N* ammonium carbonate, $(NH_4)_2CO_3$, solution. A white amorphous precipitate appears in each test tube. Heat the contents of each test tube. The amorphous precipitates are converted to crystalline precipitates. Decant the liquid and divide each precipitate into two parts. To one part add 2*N* HCl solution; to the other part, 2*N* CH_3COOH solution. The precipitates dissolve in both the hydrochloric acid and acetic acid.

2. Potassium chromate, K_2CrO_4, forms pale yellow precipitates with Ba^{2+} and Sr^{2+} ions (barium chromate, $BaCrO_4$, and strontium chromate, $SrCrO_4$), but does not form any precipitate with Ca^{2+} ions because $CaCrO_4$ is readily soluble in water.

The equations for the precipitation of barium chromate are:

$$BaCl_2 + K_2CrO_4 = BaCrO_4\downarrow + 2KCl$$

$$Ba^{2+} + CrO_4^{2-} = BaCrO_4\downarrow$$

A similar reaction takes place with strontium ions.

Barium chromate dissolves in HCl and HNO_3, but does not dissolve in acetic acid. Strontium chromate dissolves in HCl, HNO_3 and in acetic acid. The dissolving of $BaCrO_4$ in strong acids proceeds as follows:

$$2BaCrO_4 + 4HCl = 2BaCl_2 + H_2Cr_2O_7 + H_2O$$

$$2BaCrO_4 + 2H^+ = 2Ba^{2+} + Cr_2O_7^{2-} + H_2O$$

Procedure. In one test tube place 3-5 drops of a solution of a barium salt; in another, a strontium salt; in a third, a calcium salt. To each test tube add 3-5 drops of $2N$ K_2CrO_4 solution. A pale yellow precipitate is formed in the test tubes with Ba^{2+} and Sr^{2+} ions, whereas no precipitate is formed in the test tube with Ca^{2+} ions. Divide each precipitate into two parts: to one of them add HCl or HNO_3, to the other, CH_3COOH. Barium chromate dissolves in the HCl or HNO_3 but does not dissolve in CH_3COOH. Strontium chromate dissolves in HCl or HNO_3 and also in CH_3COOH.

3. Potassium dichromate, $K_2Cr_2O_7$, yields with Ba^{2+} a scanty pale yellow precipitate, $BaCrO_4$[1], but does not form any precipitate with Sr^{2+} and Ca^{2+} ions. The equations for the reaction are:

$$2BaCl_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4 + 2KCl + 2HCl$$

$$2Ba^{2+} + 4Cl^{2-} + 2K^+ + Cr_2O_7^{2-} + H_2O \rightleftarrows$$

$$\rightleftarrows 2BaCrO_4 + 2H^+ + 4Cl^- + 2K^+$$

$$2Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftarrows 2BaCrO_4 + 2H^+$$

The strong acid formed as a result of this reaction partly dissolves the barium chromate and, consequently, it is not precipitated completely. For complete precipitation of $BaCrO_4$ it is necessary to reduce the dissolving action of the strong acid. This is achieved by adding sodium acetate to the solution under test. As a result the following reaction occurs:

$$HCl + CH_3COONa = NaCl + CH_3COOH$$

$$H^+ + CH_3COO^- = CH_3COOH$$

Thus, instead of the strong acid, a weak acetic acid is formed, in which $BaCrO_4$ does not dissolve.

Strontium ions do not form a precipitate with potassium dichromate even in the presence of an acetate of an alkali metal because the $SrCrO_4$ formed is soluble in both strong acids and in acetic acid.

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[1] Most dichromates are readily soluble in water. However, on mixing a dichromate of an alkali metal with a solution of a salt of a metal whose dichromate is readily soluble whilst the chromate is sparingly soluble, the chromate of the corresponding metal is precipitated as a result of hydrolysis of the dissolved dichromate.

Thus, potassium dichromate in the presence of sodium acetate, or potassium chromate in an acetic acid solution is used for identifying the barium ion.

Procedure. To solutions of barium and strontium salts contained in two separate test tubes add 3-5 drops of potassium dichromate solution. A small precipitate will be formed with barium ions. To the contents of each test tube add 3-5 drops of 2*N* CH_3COONa solution. The precipitate of $BaCrO_4$ will become larger, while no precipitate is formed in the test tube with the strontium salt.

4. Sulphuric acid and its salts form with Ba^{2+} and Sr^{2+} salts white crystalline precipitates of the sulphates, $BaSO_4$, and $SrSO_4$. Calcium sulphate is precipitated only from concentrated solutions and a crystalline hydrated sulphate of calcium, $CaSO_4 \cdot 2H_2O$, is formed, which is partly dissolved in water (2.0 g/lit at 20°C).

Barium sulphate is sparingly soluble in water (2-3 mg/lit). Therefore, sulphuric acid is a very sensitive reagent for Ba^{2+} ions; Sr^{2+} and Ca^{2+} ions interfere with this test as they also form precipitates with sulphuric acid.

The sulphates of alkaline earth metals are insoluble in weak acids as well as in strong acids.

Procedure. Place 3-5 drops of a barium salt solution in a test tube; the same amount of a strontium salt solution in a second test tube; and a calcium salt solution in a third test tube. To the contents of each test tube add 2 or 3 drops of 2*N* H_2SO_4 solution. Voluminous white precipitates will appear in the test tubes with Ba^{2+} and Sr^{2+} ions, whereas in the test tube with Ca^{2+} ions no precipitate at all or a very scanty one will appear. Divide each precipitate into two parts and to one of them add 2*N* HCl solution; to the other, 2*N* CH_3COOH solution. The precipitates will dissolve neither in hydrochloric acid nor in acetic acid.

5. Ammonium sulphate, $(NH_4)_2SO_4$. A saturated solution of this salt precipitates barium and strontium ions, but does not precipitate calcium ion because the latter forms a soluble complex salt, $(NH_4)_2[Ca(SO_4)_2]$. The equations for the reaction of Ca^{2+} ion with a saturated solution of ammonium sulphate are

$$Ca^{2+} + SO_4^{2-} = CaSO_4$$

$$CaSO_4 + (NH_4)_2SO_4 = (NH_4)_2[Ca(SO_4)_2]$$

Procedure. To 3-5 drops of the solutions of barium, strontium, and calcium salts contained in three different test tubes add 5-8 drops of saturated $(NH_4)_2SO_4$. In the test tube with the calcium salt no precipitate will appear, whereas in the test tubes with Ba^{2+} and Sr^{2+} ions voluminous precipitates of barium and strontium sulphates will be formed.

6. A saturated solution of gypsum ($CaSO_4 \cdot 2H_2O$) on reacting with Ba^{2+} ions in the cold immediately precipitates $BaSO_4$. On reacting with Sr^{2+} ions it produces a slight turbidity only after heating the mixture or in the cold after standing for a long time.

A saturated solution of gypsum does not form precipitates in solutions of calcium salts in the cold or even on heating. This distinguishes Ca^{2+} ions from Ba^{2+} and Sr^{2+} ions.

Procedure. To 3 or 4 drops of solutions of barium, strontium, and calcium salts contained in separate test tubes add 3-5 drops of a saturated solution of gypsum. In the test tube with the barium salt, a small precipitate will appear at once; in the test tube with the strontium salt a slight turbidity will appear only after heating; in the test tube with the calcium salt no turbidity will appear at all, either in the cold or on heating.

7. Ammonium oxalate, $(NH_4)_2C_2O_4$, forms with ions of the alkaline earth metals white crystalline precipitates of BaC_2O_4, SrC_2O_4, and CaC_2O_4:

$$BaCl_2 + (NH_4)_2C_2O_4 = BaC_2O_4\downarrow + 2NH_4Cl$$

$$Ba^{2+} + C_2O_4^{2-} = BaC_2O_4\downarrow$$

The reactions with Ca^{2+} and Sr^{2+} proceed likewise. An oxalic acid solution precipitates Ca^{2+} ions from a neutral solution, but does not precipitate Ba^{2+} and Sr^{2+} ions.

The oxalates of all the alkaline earth metals dissolve in $2N$ HCl and HNO_3 solutions, and do not dissolve in the cold in $2N$ CH_3COOH solution.

The equations for the reaction of BaC_2O_4 with strong acids are:

$$BaC_2O_4 + 2HCl = BaCl_2 + H_2C_2O_4$$

$$BaC_2O_4 + 2H^+ = Ba^{2+} + H_2C_2O_4$$

In boiling acetic acid, barium oxalate and strontium oxalate dissolve, whereas calcium oxalate does not dissolve.

Procedure. To solutions containing barium, strontium, and calcium salts contained in separate test tubes add 3-5 drops of $2N$ $(NH_4)_2C_2O_4$ solution. A white crystalline precipitate will appear in all the test tubes. Divide each precipitate into two parts: to one add $2N$ HCl solution; to the other add CH_3COOH solution. All the precipitates will dissolve in hydrochloric acid and not dissolve in acetic acid in the cold. On boiling, however, barium and strontium oxalates dissolve in acetic acid, whereas calcium oxalate does not.

8. Sodium rhodizonate, $Na_2C_6O_6$, forms a red precipitate with Ba^{2+} ions and a brownish-red precipitate with Sr^{2+} ions. Barium rhodizonate is not decolourized by the action of $2N$ HCl solution, while strontium rhodizonate is decolourized. Therefore, this reagent is used to detect Ba^{2+} and Sr^{2+} ions.

Procedure. Place a drop of the solution under test (a neutral solution or one to which a weak hydrochloric acid solution has been added) on a strip of filter paper and wet the resulting spot with 0.1 per cent aqueous sodium rhodizonate solution. In the presence of barium a red spot will appear. Wet this spot with $2N$ HCl solution. The spot will not be decolourized. In the presence of strontium, the spot will be a brownish-red colour that disappears on adding $2N$ HCl solution.

Sodium rhodizonate can be used to detect strontium ions in the presence of barium ions as follows. Moisten a strip of filter paper with K_2CrO_4 solution and allow to dry. Apply a drop of the solution under test to it to form a chromate precipitate. In 1-2 minutes add a drop of 0.1 per cent aqueous sodium rhodizonate solution. In the presence of strontium a brownish-red spot will appear, which is decolourized by the action of $2N$ HCl solution; barium ions under these conditions do not react with sodium rhodizonate and therefore do not interfere with the detection of strontium ions.

9. Flame test. Clean a platinum or nichrome wire (see Sec. 24, *P* 2), heat it strongly, dip it into a test tube containing the solution of a barium salt (best of all $BaCl_2$) and introduce it into the nonluminous flame of the gas burner. The flame will assume a yellow-green colour. Make this

test with a solution of a strontium salt ($SrCl_2$ or $Sr(NO_3)_2$). The flame assumes a characteristic crimson colour visible through cobalt glass. Perform the same test with a solution of a calcium salt ($CaCl_2$ or $Ca(NO_3)_2$). The flame will assume a brick-red colour. This test is not applicable in the presence of Sr^{2+} ions.

Record the test results in a Table as shown at the beginning of the Section.

Tests for Ba^{2+}, Sr^{2+}, and Ca^{2+} Ions

Cation	Reagent: indications of presence of the given ion
Ba^{2+}	(1) K_2CrO_4 in acetic acid solution or $K_2Cr_2O_7$ + + CH_3COONa: pale yellow precipitate (2) H_2SO_4: white precipitate (Sr^{2+} and Ca^{2+} ions interfere with this test) (3) Saturated solution of gypsum: rapid formation of a small precipitate (4) Filter paper spot test with sodium rhodizonate in a neutral solution: red precipitate that is not decolourized by 2*N* HCl solution (5) Flame test: yellowish-green colour
Sr^{2+} (in the absence of Ba^{2+})	(1) $(NH_4)_2SO_4$: abundant white precipitate (2) Saturated solution of gypsum: slight turbidity on heating (3) Filter paper spot test with sodium rhodizonate: a brownish-red precipitate that is decolourized by 2*N* HCl solution (4) Flame test: crimson coloration (the presence of Ba^{2+} and Ca^{2+} ions does not interfere with this test)
Ca^{2+} (in the absence of Ba^{2+} and Sr^{2+})	(1) $(NH_4)_2C_2O_4$ in an acetic acid solution: white crystalline precipitate (2) 1*N* $H_2C_2O_4$ solution in a neutral solution: white crystalline precipitate (3) Flame test: brick-red colour

36. Analysis of Mixture of Cations of Groups I and II in the Absence of Sulphates

The Group II cations present in a solution of their salts are separated from the Group I cations by means of ammonium carbonate. This reagent, however, under ordinary conditions precipitates Mg^{2+} ions as well as Group II cations. But in the presence of even small quantities of ammonium salts, Mg^{2+} is not precipitated by ammonium carbonate, whereas barium, strontium, and calcium carbonates are precipitated by this reagent even in the presence of small amounts of other ammonium salts because the solubility product of $BaCO_3$, $SrCO_3$, and $CaCO_3$ is 10,000 times less than the solubility product of $MgCO_3$.

Commercial ammonium carbonate is contaminated with ammonium carbamate, NH_4OCONH_2, and ammonium bicarbonate, NH_4HCO_3. The latter is produced as a result of the hydrolysis of $(NH_4)_2CO_3$:

$$(NH_4)_2CO_3 + H_2O \rightleftarrows NH_4HCO_3 + NH_4OH$$
$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$$

On adding ammonia solution to the ammonium bicarbonate solution, the latter is converted to the carbonate:

$$NH_4HCO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O$$
$$NH_4^+ + HCO_3^- + NH_4OH = 2NH_4^+ + CO_3^{2-} + H_2O$$

On heating an aqueous solution of ammonium carbonate, NH_4OCONH_2 is converted to ammonium carbonate:

$$NH_4OCONH_2 + H_2O = (NH_4)_2CO_3$$

Thus, for complete precipitation of Group II cations with ammonium carbonate it is necessary to proceed as follows: add ammonia solution to the solution under test until the reaction is alkaline (to convert NH_4HCO_3 to $(NH_4)_2CO_3$) and NH_4Cl solution (to avoid precipitation of $Mg(OH)_2$).

To obtain granular precipitates of carbonates of the alkaline earth metals, which can easily be washed and separated by centrifuging, and also to convert NH_4OCONH_2 to $(NH_4)_2CO_3$, heat the solution to a temperature not above 70-80°C because at higher temperatures $(NH_4)_2CO_3$ is decom-

posed as follows:

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O$$

To the hot solution of the mixture of cations of Groups I and II containing NH_4OH and NH_4Cl add, while stirring, $(NH_4)_2CO_3$. Only provided these conditions are observed, is it possible to separate quantitatively the cations of the alkaline earth metals from the cations of the first group (Group II cations from Group I cations).

The separation of Ba^{2+}, Sr^{2+}, and Ca^{2+} ions from each other is based on the different solubility of their sulphates and chromates.

Ba^{2+} ions are precipitated by CrO_4^{2-} ions in an acetic acid solution or by $Cr_2O_7^{2-}$ ions in the presence of acetate ions, whereas Sr^{2+} and Ca^{2+} ions under these conditions are not precipitated. Therefore, potassium chromate, K_2CrO_4, in an acetic acid solution or a mixture of $K_2Cr_2O_7$ + + CH_3COONa can be used to isolate Ba^{2+} from Ca^{2+} and Sr^{2+} ions.

The separation of Sr^{2+} ions from Ca^{2+} ions is based on the fact that a saturated $(NH_4)_2SO_4$ solution forms a precipitate with Sr^{2+} ions, but forms a soluble salt with Ca^{2+} ions.

The analysis of a mixture of cations of Groups I and II in the absence of sulphate ions[1] is carried out in the following sequence:

1. Test for ammonium ions. In all procedures of analysis of a mixture of cations, prior to adding reagents containing NH_4^+ ions, it is necessary to carry out an identification test for this ion (see Sec. 28, *P* 1) on a separate sample of the original solution.

2. Test for presence of Group II cations. Place 2 or 3 drops of the solution under test in a test tube; add 2 or 3 drops of $2N$ NH_4Cl solution, $6N$ NH_4OH solution until the solution is alkaline to litmus, and 2 or 3 drops of $2N$ $(NH_4)_2CO_3$ solution. The presence of Group II cations is indicated by the appearance of a precipitate.

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[1] To prepare such a solution yourself (for practice) place in a test tube 5-8 drops of solutions of the chlorides or nitrates of all the metals of Groups I and II.

3. Precipitation of Group II cations. To 5-8 ml of the solution under test add a few drops of $6N$ ammonia solution until the solution is alkaline to litmus and $2N$ NH_4Cl solution in such a quantity that $Mg(OH)_2$ is not precipitated. A slight turbidity may be disregarded. Then heat the mixture to boiling and, stirring constantly with a glass rod, add to the hot solution $2N$ $(NH_4)_2CO_3$ solution drop by drop until precipitation of the carbonates is complete. This takes some time. To check for completeness of precipitation, heat the mixture on a small burner flame for 2-3 minutes, shaking constantly, and centrifuge.

4. Test for completeness of precipitation. Without decanting the solution, carefully add to the clear supernatant liquid, down the walls of the test tube, a few drops of $(NH_4)_2CO_3$ solution. If the liquid remains clear, precipitation of Group II ions is complete. If a precipitate or turbidity appears, heat the mixture to boiling, add 5-8 drops of $(NH_4)_2CO_3$ solution, centrifuge, and check for completeness of precipitation once more.

5. Separation of Group II cations from Group I cations. After making sure that precipitation is complete, separate precipitate 1 from supernatant 1.

Precipitate 1: Group II carbonates; analyze as described in *P* 7 et seq.

Supernatant 1: Group I cations, an excess of $(NH_4)_2CO_3$, and other ammonium salts; analyze as described in *P* 6.

6. Preparation of supernatant 1 for detection of Group I cations. Heat supernatant 1 to the boiling point, add 3 or 4 drops of $2N$ $(NH_4)_2C_2O_4$ solution. Mix thoroughly with a glass rod, heat to boiling again, and allow to settle for 3-5 minutes. Centrifuge the mixture; discard the precipitate containing traces of Group II cations and test for Group I cations in the clear supernatant (as described in Sec. 28, *P* 2 to *P* 7).

7. Dissolving of the Group II carbonates. Wash precipitate 1 with hot water and add 3-5 ml of previously heated $4N$ acetic acid solution to the test tube containing the precipitate. Dissolve the precipitate by heating it in acetic acid, thoroughly mixing the contents of the test tube with a glass rod. If the precipitate fails to dissolve, add a few

more drops of $4N$ acetic acid solution. The resulting solution contains the Group II acetates.

8. Test for barium ions. To 2 or 3 drops of the acetic acid solution obtained above add 2 or 3 drops of $1N$ K_2CrO_4 solution and heat to boiling. The appearance of a precipitate indicates the presence of barium ions. In this case continue the analysis as described in *P* 9. If no precipitate is formed (Ba^{2+} ions are absent), analyze the solution as described in *P* 11.

9. Isolation of barium ions. Heat the rest of the solution obtained in *P* 7 to the boiling point. Add $1N$ K_2CrO_4 solution slowly, drop by drop, stirring the mixture with a glass rod, until the supernatant liquid assumes an orange colour. In an acidic solution, the yellow chromate ion is converted to the orange dichromate ion. Heat the mixture to boiling once more and, without allowing it to cool, centrifuge to separate precipitate 2 containing barium chromate from supernatant 2 containing Sr^{2+}, Ca^{2+}, and $Cr_2O_7^{2-}$ ions and acetic acid.

Precipitate 2: barium chromate; is not analyzed.

Supernatant 2: strontium, calcium, and dichromate ions and acetic acid; analyze as described in *P* 10 et seq.

10. Separation of strontium and calcium ions from dichromate ions. Heat supernatant 2 to the boiling point, add $2N$ Na_2CO_3 solution drop by drop until the solution is alkaline; this is indicated by the change in colour of the solution from orange (dichromate ion, $Cr_2O_7^{2-}$) to yellow (chromate ion, CrO_4^{2-}). Heat the mixture to the boiling point, stirring constantly. Allow it to cool during 3-5 minutes and centrifuge. Discard the supernatant and wash precipitate 3, containing strontium and calcium carbonates, with hot water until the wash water and precipitate become colourless. Dissolve the washed precipitate with hot $4N$ acetic acid solution. Analyze the resulting solution containing strontium and calcium acetates as described in *P* 11 and *P* 12.

11. Detection and isolation of strontium ions. Add 1-2 ml of saturated $(NH_4)_2SO_4$ solution to the solution obtained above. Heat the mixture to the boiling point. The appearance of a precipitate indicates the presence of strontium ions. Centrifuge the mixture and test for Ca^{2+} ions in the supernatant.

12. Test for calcium ions. To 1 ml of the supernatant heated to the boiling point, add 0.5 ml of 2*N* $(NH_4)_2C_2O_4$ solution. Allow the precipitate to settle during 3-5 minutes. The formation of a white precipitate that does not dissolve on heating in acetic acid shows that Ca^{2+} ions are present.

37. Scheme for Analysis of the Group II Carbonates in the Absence of Sulphates

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$
Add 2*N* CH_3COOH to dissolve. Add $K_2Cr_2O_7 + CH_3COONa$. Sec. 36, *P* 7,9

Precipitate: $BaCrO_4$ (yellow)	*Solution*: Ca^{2+} and Sr^{2+}
Confirmatory test: Dissolve the precipitate in HCl. Add H_2SO_4 to a portion of the resulting solution. A white precipitate, $BaSO_4$, appears	To a portion of the solution add saturated $(NH_4)_2SO_4$ solution. Sec. 36, *P* 11. The formation of a precipitate will show that Sr^{2+} ions are present. Centrifuge and test for Ca^{2+} by adding $(NH_4)_2C_2O_4$. Sec. 36, *P* 12

Review Questions

1. Why are NH_4OH and NH_4Cl added, in addition to ammonium carbonate, when separating Group II cations from Group I cations?
2. Why are the Group II carbonates formed in the course of the analysis dissolved in acetic acid and not in hydrochloric acid?
3. What identification tests do you know for Ba^{2+}, Ca^{2+}, and Sr^{2+} ions?
4. Why does $BaCO_3$ dissolve in HCl and CH_3COOH, whereas $BaSO_4$ is not soluble in these acids?
5. Why is a voluminous precipitate formed in the reaction between Ba^{2+} and H_2SO_4, while a scanty one is formed in the reaction between Ba^{2+} and $CaSO_4 \cdot 2H_2O$?

38. Analysis of Mixture of Cations of Groups I and II in the Presence of Sulphates

The sulphates of the alkaline earth metals are insoluble in water and in dilute acids. Therefore, in the presence of SO_4^{2-} ions the solution under test will contain a precipi-

tate[1]. If the sample containing sulphates of alkaline earth metals is in the solid state, it does not dissolve completely in water or acids.

To dissolve the sulphates, they are first converted to the corresponding carbonates which are then dissolved in acids. The Group II sulphates are converted to the carbonates by boiling or fusing with carbonates of the alkali metals; the following reaction takes place:

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4$$

This is a reversible reaction and therefore to convert the sulphate to the corresponding carbonate it is necessary to add an excess of the carbonate of the alkali metal.

The analysis is carried out in the following order:

1. Test for presence of Group II sulphates. Shake the mixture under test thoroughly, take 5-8 drops and add 1-2 ml of $2N$ HNO_3 or HCl solution. Heat the mixture to boiling. If the precipitate does not dissolve, Group II sulphates are present; if it does dissolve, sulphates are absent.

2. Precipitation of the Group II sulphates. To 3-5 ml of the suspension (turbid mixture) under test add 5 or 6 drops of $2N$ HNO_3 or HCl solution, heat the mixture to boiling and slowly add, while shaking, $4N$ H_2SO_4 solution drop by drop. Heat the mixture to the boiling point once more but do not allow to boil, remove it from the flame, and let it stand for 1-2 minutes.

3. Test for completeness of precipitation of sulphates. Pour 2 or 3 drops of $4N$ H_2SO_4 solution down the walls of the small flask or beaker. No turbidity should appear. After making sure that precipitation is complete, allow the mixture to settle and separate the precipitate from the solution by centrifuging or carefully decanting.

Precipitate 1: Group II cations; analyze as described in *P* 5 et seq.

Supernatant 1: Group I cations and, possibly, calcium sulphate ions; analyze as described in *P* 4.

4. Test for calcium ions and Group I cations. To 1 ml of supernatant 1 add $2N$ NH_4OH until the solution is alkaline

[1] Because of its considerable solubility, calcium sulphate may also be partially dissolved in the solution.

to litmus, then add acetic acid to make the solution acidic to litmus or indicator paper (pH = 3-4). Heat the resulting acidic solution to boiling and add 1-2 ml of 2*N* solution of ammonium oxalate, $(NH_4)_2C_2O_4$, to it. The presence of calcium ions is indicated by the formation of a precipitate. If no precipitate is formed, transfer the solution to an evaporating dish, evaporate the ammonium salts, and test for Group I cations (see Sec. 28). In case a precipitate is formed, to supernatant 1 add 2*N* NaOH solution until the solution is alkaline and then 2*N* CH_3COOH solution until the solution is acidic. Heat the mixture to boiling and add to it 1-2 ml of 2*N* $(NH_4)_2C_2O_4$ solution. Centrifuge the mixture, discard the precipitate, and test the supernatant for the presence of Group 1 cations (see Sec. 28).

5. Washing of Group II sulphates. It is necessary to wash precipitate 1 to free it from excess SO_4^{2-} ions. For this purpose transfer it to a beaker or evaporating dish and add 3-5 ml of hot water to it. Stir the mixture thoroughly, allow it to settle, and separate the precipitate from the solution by centrifuging or carefully decanting the liquid. Wash the precipitate 3 or 4 times with hot water.

6. **Test for completeness of washing.** To 2-3 ml of the wash water add 1-2 ml of 2*N* HCl solution and 1 ml of $BaCl_2$. If no precipitate or turbidity appears, completeness of washing has been achieved.

7. Conversion of the Group II sulphates to carbonates. Transfer the washed precipitate to an evaporating dish or beaker, add 5-6 ml of 4*N* Na_2CO_3 solution and boil, stirring constantly, over a small flame for 3-5 minutes. Transfer the mixture to a centrifuge tube and centrifuge. Analyze precipitate 2 as described in *P* 8; discard the supernatant.

8. Analysis of precipitate 2. To free the precipitate from SO_4^{2-} ions it is necessary to wash it 3 or 4 times with hot water (see *P* 5). Check for completeness of washing as follows: to 1-2 ml of the wash water add 3-5 drops of 2*N* $BaCl_2$ solution and 1-2 ml of 2*N* HNO_3 solution. If no precipitate is formed, completeness of washing is indicated. If a precipitate is formed that does not dissolve in HNO_3, continue washing. Only after making sure that washing is complete, dissolve the precipitate in hot 4*N* acetic acid. Test the resulting solution for Group II cations (see Sec. 36, *P* 7 et seq.).

CHAPTER X

Hydrogen Ion Concentration

39. Hydrogen Ion Concentration in Water

Water dissociates, although to a very small degree, according to the following equation:

$$H_2O \rightleftarrows H^+ + OH^-$$

The equilibrium constant of this reaction is

$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad (1)$$

where $[H^+]$ and $[OH^-]$ = concentration of hydrogen and hydroxyl ions, respectively, gram-ions per litre

$[H_2O]$ = concentration of undissociated molecules, moles per litre

K = dissociation constant of water

From equation (1) we can derive the new equation

$$[H^+][OH^-] = K\,[H_2O] \quad (2)$$

Since the dissociation of water is very insignificant, the concentration of $[H^+]$ and $[OH^-]$ is very small. One litre of water contains $\frac{1,000}{18}$, i.e., 55.5 moles of water. At room temperature only 10^{-7} moles of water dissociate (0.0000001). Hence, the concentration of undissociated molecules is equal to 55.5 — 0.0000001 moles. Since 0.0000001 is a negligible quantity it can be assumed that the concentration of undissociated molecules of water is equal to 55.5 moles.

On increasing the concentration of H^+ ions in water (by adding an acid) or the concentration of OH^- ions (by adding an alkali) the concentration of dissociated molecules of water, due to the addition of a common ion, becomes less than 10^{-7}. Therefore, the concentration of undissociated molecules in an acid or alkaline solution can be taken to be 55.5 moles with even less error than in a neutral solution. It follows that the concentration of undissociated molecules of water in any aqueous solution should be taken as a constant value. Hence, the right-hand side of equation (2) is the product of two con-

stants, i.e., is also a constant. In consequence, the left-hand side of the equation is also a constant value.

Denoting the product $K[H_2O]$ by the symbol K_{H_2O}, we have the following equation for the new constant:

$$[H^+][OH^-] = K_{H_2O} \tag{3}$$

The product of the concentrations of the hydrogen and hydroxyl ions, K_{H_2O}, is termed the *ionic product of water.*

At room temperature $K_{H_2O} \approx 10^{-14}$. In this case equation (3) can be written as follows:

$$[H^+][OH^-] = 10^{-14} \tag{4}$$

In any aqueous solution the product of the concentrations of the hydrogen and hydroxyl ions is equal to 10^{-14}.

In a perfectly neutral solution and in pure water the concentration of hydrogen ions is equal to the concentration of hydroxyl ions:

$$[H^+] = [OH^-] = 10^{-7} \text{ g-ion/lit}$$

The addition of an acid to water increases the concentration of hydrogen ions and, at the same time, decreases the concentration of hydroxyl ions, since the ionic product of water remains constant. The addition of an alkali, on the contrary, results in a decrease of the concentration of hydrogen ions.

In any aqueous solution of an acid, base, or salt there are always hydrogen and hydroxyl ions present. If $[H^+] > 10^{-7}$ g-ion/lit (for example, 10^{-5}), the solution is acidic. In an alkaline solution $[H^+] < 10^{-7}$ g-ion/lit (for example, 10^{-8}) and $[OH^-] > 10^{-7}$ g-ion/lit.

In a neutral solution $[H^+] = 10^{-7}$; *in an acidic solution* $[H^+] > 10^{-7}$; *in an alkaline solution* $[H^+] < 10^{-7}$.

If the concentration of one of the ions is known, the concentration of the other ion can be calculated by using equation (4):

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} \qquad \text{and} \qquad [H^+] = \frac{K_{H_2O}}{[OH^-]}$$

Example. The concentration of hydrogen ions in an aqueous solution equals $2 \cdot 10^{-5}$ g-ion/lit. Calculate the concentration of hydroxyl ions.

Solution. $[OH^-] = \frac{10^{-14}}{2 \cdot 10^{-5}} = \frac{10 \cdot 10^{-15}}{2 \cdot 10^{-5}} = 5 \cdot 10^{-10}$ g-ion/lit

The ionic product of water varies with the temperature of the solution as can be seen from the following data:

Temperature of solution, °C	0	10	25	50	100
Ionic product of water K_{H_2O}	$0.12 \cdot 10^{-14}$	$0.3 \cdot 10^{-14}$	$1.2 \cdot 10^{-14}$	$8.0 \cdot 10^{-14}$	$73.0 \cdot 10^{-14}$

Review Questions

1. Define the term *ionic product of water.*
2. What is the concentration of hydrogen ions in a neutral, in an acidic, in an alkaline solution?
3. The concentration of hydrogen ions in a given aqueous solution equals 10^{-5}. Determine: (a) whether the solution is neutral, acidic, or alkaline; (b) the concentration of hydroxyl ions in the solution; (c) whether an acid or alkaline must be added to this solution in order to bring the concentration of hydrogen ions to 10^{-3}.

40. pH-Value and pOH-Value

The hydrogen ion and hydroxyl ion concentrations are usually expressed as the negative logarithm of their concentration and are denoted by the symbols pH and pOH.

$$pH = -\log [H^+]; \quad pOH = -\log [OH^-]$$

The pH-value is used to express the acidity of a solution; the pOH-value, the alkalinity of a solution.

The pH can be determined if the hydrogen ion concentration is known, and vice versa. In neutral solutions $[H^+] = 10^{-7}$. The logarithm of this expression is:

$$\log [H^+] = \log 10^{-7} = -7 \log 10$$

On changing the signs we have

$$-\log [H^+] = 7; \quad pH = -\log [H^+] = 7$$

Hence, in a neutral solution pH = 7. In an acidic solution $[H^+] > 10^{-7}$ (for example, 10^{-3}) and the pH < 7 (in

the given solution pH = 3). In an alkaline solution $[H^+] < 10^{-7}$ (for example, $[H^+] = 10^{-9}$); pH > 7 (in the given example pH = 9).

Since in a neutral solution $[H^+] = 10^{-7}$, in an acidic solution $[H^+] > 10^{-7}$, and in an alkaline solution $[H^+] < 10^{-7}$, it follows that in a neutral solution pH = 7, in an acidic solution pH < 7, and in an alkaline solution pH > 7.

This can be presented as follows:

	Increase in acidity	Neutral solution	Increase in alkalinity
pH	← 0 1 2 3 4 5 6	7	→ 8 9 10 11 12 13 14

The ionic product of water $K_{H_2O} = [H^+]\,[OH^-] = 10^{-14}$. On taking the logarithm of this equation, we have

$$\log [H^+] + \log [OH^-] = \log [10^{-14}] = -14$$

Hence,

$$-\log [H^+] - \log [OH^-] = 14 \qquad (1)$$

Since $-\log [H^+] = pH$; $-\log [OH^-] = pOH$, by substituting these values in equation (1), we have

$$pH + pOH = 14 \qquad (2)$$

whence

$$pH = 14 - pOH \quad \text{and} \quad pOH = 14 - pH$$

The concentration of hydrogen ions can be calculated from a known value of the pH or pOH.

Example 1. Calculate the hydrogen ion concentration if the pH of the solution equals 6.7.

Solution. pH = 6.7; $-\log [H^+] = 6.7$; $\log [H^+] = -6.7 = \overline{7}.3$; hence, $[H^+] = 2 \cdot 10^{-7}$.

Example 2. Calculate the hydrogen ion and hydroxyl ion concentrations if pOH = 4.34.

Solution. pH = 14 − 4.34 = 9.66

Hence, $\log [H^+] = -9.66 = \overline{10}.34$ and $[H^+] = 2.2 \cdot 10^{-10}$

$[OH^-]$ can be calculated in two ways:

(a) $[OH^-] = \frac{K_{H_2O}}{[H^+]} = \frac{10^{-14}}{2.2 \cdot 10^{-10}} = 4.5 \cdot 10^{-5}$

(b) if pOH = 4.34, $\log [OH^-] = -4.34 = \bar{5}.66$

Hence, $[OH^-] = 4.5 \cdot 10^{-5}$

Problems

1. Calculate the pH and $[OH^-]$ of solutions in which $[H^+]$ equals: (a) $4 \cdot 10^{-3}$; (b) $1.5 \cdot 10^{-7}$; (c) $1.3 \cdot 10^{-3}$.
Ans. (a) 2.4; $2.5 \cdot 10^{-12}$ g-ion/lit
2. Calculate $[H^+]$ and pH of solutions if $[OH^-]$ equals: (a) $5.8 \cdot 10^{-4}$; (b) $3.2 \cdot 10^{-6}$; (c) $7.5 \cdot 10^{-9}$.
Ans. (a) $1.7 \cdot 10^{-11}$ g-ion/lit; 10.77
3. Calculate $[H^+]$ and $[OH^-]$ if the pH of the solutions equals: (a) 4.3; (b) 7.8; (c) 9.64.
Ans. (a) $5 \cdot 10^{-5}$; $2 \cdot 10^{-10}$ g-ion/lit
4. Calculate $[H^+]$, $[OH^-]$, and pH of solutions in which the pOH equals: (a) 8.34; (b) 5.86.
Ans. (a) $2.2 \cdot 10^{-6}$ g-ion/lit; $4.5 \cdot 10^{-9}$ g-ion/lit; pH = 5.66.

41. Hydrogen Ion Concentration in Aqueous Solutions of Acids and Alkalies

Hydrogen ion concentration in solutions of strong monobasic acids. The halogen acids (HCl, HBr, HI), nitric acid, HNO_3, perchloric acid, $HClO_4$, and chloric acid, $HClO_3$, are strong monobasic acids.

The equation for dissociation of a strong monobasic acid is

$$HA \rightarrow H^+ + A^-$$

Since strong acids can be considered to dissociate completely in aqueous solutions, the hydrogen ion concentration is equal to the concentration of the given acid:

$$[H^+] = C_{acid} \qquad (1)$$

where C_{acid} is the molar concentration of the acid.

Thus, in dilute solutions of strong monobasic acids the hydrogen ion concentration expressed in gram-ions per litre is equal to the concentration of the acid in moles per litre or in gram-equivalents per litre (for monobasic acids these quantities are the same).

Example. Determine the hydrogen ion concentration $[H^+]$ and pH in 0.05*N* HCl solution.

Solution. Since $[H^+] = C_{acid}$, and $C_{acid} = 0.05$ mole/lit,

$$[H^+] = 0.05 = 5 \cdot 10^{-2}$$

$$pH = -\log [H^+] = -\log 5 \cdot 10^{-2} = -(\log 5 - 2 \log 10) =$$

$$= -\log 5 + 2$$

Since

$$\log 5 = 0.70, \quad pH = 2 - 0.70 = 1.30$$

Hydrogen ion concentration in solutions of weak monobasic acids. Let us denote the acid as HA; its concentration, as C_{HA}; the hydrogen ion and anion concentrations as $[H^+]$ and $[A^-]$, respectively; the concentration of undissociated molecules as HA; and the dissociation constant as K_{acid}.

The equation for the dissociation of the acid is

$$HA \rightleftarrows H^+ + A^-$$

The dissociation constant is

$$K_{acid} = \frac{[H^+][A^-]}{[HA]} \tag{2}$$

Let us denote the concentration of dissociated molecules of the acid as x, then for a monobasic acid $[H^+] = [A^-] = x$. The concentration of undissociated molecules $HA = C_{acid} - x$. In solutions of very weak acids the concentration of dissociated molecules x is negligible as compared with the total concentration C_{acid}; therefore, the difference $C_{acid} - x$ can be taken as equal to C_{acid}. Then, using equation (2), we obtain

$$K_{acid} = \frac{x^2}{C_{acid}}$$

Hence,

$$x = \sqrt{K_{acid} \cdot C_{acid}} \quad \text{and} \quad [H^+] = \sqrt{K_{acid} \cdot C_{acid}} \tag{3}$$

Example. Calculate the hydrogen ion concentration and pH of 0.2*N* CH_3COOH solution.

Solution

$$[H^+] = \sqrt{K_{CH_3COOH} \cdot C_{CH_3COOH}}$$

Since $K_{CH_3COOH} = 1.74 \cdot 10^{-5}$ and $C_{CH_3COOH} = 0.2$ (by statement of the problem) then $[H^+] = \sqrt{1.74 \cdot 10^{-5} \cdot 0.2} = \sqrt{0.348 \cdot 10^{-5}} = \sqrt{3.48 \cdot 10^{-6}} = 1.9 \cdot 10^{-3}$; $pH = 3 - \log 1.9 = 3 - 0.28 = 2.72$

Hydrogen ion concentration in solutions of weak monobasic acids in the presence of salts of the same acid. Dissociation of a weak acid and its salt (MeA) is expressed by the following equations:

$$HA \rightleftarrows H^+ + A^-; \qquad MeA \rightarrow Me^+ + A^-$$

The dissociation constant of the acid is

$$K_{acid} = \frac{[H^+][A^-]}{[HA]} \tag{4}$$

The concentration of the anion $[A^-]$ is equal to the sum of the concentrations of the anions of the salt and the acid. Since the concentration of the anions formed on dissociation of a weak acid is very small, it can be disregarded and the concentration of anions, $[A^-]$, can be taken to be equal to the concentration of the salt, i.e., $[A^-] = C_{salt}$.

The concentration of the undissociated molecules of a weak acid can, with sufficient accuracy, be assumed to be equal to the total concentration of the acid. Consequently,

$$[HA] = C_{acid}$$

Substituting these values in equation (4), we obtain

$$K_{acid} = \frac{[H^+] \cdot C_{salt}}{C_{acid}}$$

and, therefore,

$$[H^+] = K_{acid} \cdot \frac{C_{acid}}{C_{salt}} \tag{5}$$

Example. Calculate the hydrogen ion concentration and pH of a solution containing in 1 litre 0.03 mole of CH_3COOH and 0.01 mole of CH_3COONa ($K_{CH_3COOH} = 1.74 \cdot 10^{-5}$).

Solution. The hydrogen ion concentration is determined from the equation

$$[H^+] = K_{acid} \cdot \frac{C_{acid}}{C_{salt}}$$

Substituting the corresponding values for the dissociation constant of acetic acid, its concentration, and the concentration of sodium acetate, we obtain

$$[H^+] = 1.74 \cdot 10^{-5} \cdot \frac{0.03}{0.01} = 1.74 \cdot 10^{-5} \cdot 3 = 5.22 \cdot 10^{-5}$$

$$pH = 5 - \log 5.22 = 5 - 0.72 = 4.28$$

Hydrogen ion concentration in solutions of weak polybasic acids. Two- and polybasic acids dissociate in several stages, for example:

$$\text{first stage: } H_2A \rightleftarrows H^+ + HA^-$$
$$\text{second stage: } HA^- \rightleftarrows H^+ + A^{2-}$$

In solution of two- and polybasic acids there are several cases of equilibrium corresponding to the different stages of dissociation, each of which has its individual dissociation constant.

The dissociation constant of the first and second stages are, respectively, equal to

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]}; \qquad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

The values K_1 and K_2 are termed the first and second dissociation constants of the acid. For example, the dissociation constants of carbonic acid are:

$$K_1 = K_{H_2CO_3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \cdot 10^{-7}$$

$$K_2 = K_{HCO_3^-} = \frac{[H^+][CO_3^{2-}]}{[HCO_3]} = 4.8 \cdot 10^{-11}$$

When determining the hydrogen ion concentration in solutions of polybasic acids, usually only the first stage of dissociation is considered if its constant is more than 1,000 times greater than the dissociation constant of the acid in the subsequent stages. In this case, all that has been said concerning monobasic acids applies to polybasic acids as well.

Example. Calculate the hydrogen ion concentration in a $0.025M$ H_2S solution if $K_{H_2S} = 8.9 \cdot 10^{-8}$; $K_{HS^-} = 1.3 \cdot 10^{-13}$.

Solution. All the hydrogen ions are produced as a result of the first stage of dissociation of hydrogen sulphide:

$$H_2S \rightleftarrows H^+ + HS^-$$

$$K_{H_2S} = \frac{[H^+][HS^-]}{[H_2S]}; \qquad [H_2S] = 0.025$$

$$[H^+] = [HS^-] = x$$

Hence,

$$K_{H_2S} = \frac{x^2}{0.025}$$

$$x = \sqrt{8.9 \cdot 10^{-8} \cdot 0.025} = \sqrt{22.25 \cdot 10^{-10}} = 4.72 \cdot 10^{-5}$$

and, consequently, $[H^+] = [HS^-] = 4.72 \cdot 10^{-5}$ g-ion/lit

Hydrogen and hydroxyl ion concentrations, pH and pOH, in alkali solutions[1]. The hydroxyl ion concentration in alkali solutions and in solutions of weak bases is calculated in the same way as the hydrogen ion concentration in acidic solutions.

Let us denote the base as MeOH, the dissociation constant as K_{base}, its concentration as C_{base}.

In an aqueous solution of a strong alkali the hydroxyl ion concentration is equal to the concentration of the alkali:

$$[OH^-] = C_{base} \tag{6}$$

In an aqueous solution of a weak base corresponding to a univalent metallic cation Me^+, the hydroxyl ion concentration equals

$$[OH^-] = \sqrt{K_{base} \cdot C_{base}} \tag{7}$$

In an aqueous solution of a weak base in the presence of its salt the hydroxyl ion concentration equals

$$[OH^-] = K_{base} \cdot \frac{C_{base}}{C_{salt}} \tag{8}$$

Example 1. Calculate $[OH^-]$ and pH of $0.05N$ NaOH solution.

Solution.

$$[OH^-] = C_{NaOH} = 0.05 = 5 \cdot 10^{-2}$$

$$pOH = 2 - \log 5 = 2 - 0.70 = 1.30; \qquad pH = 14 - 1.3 = 12.7$$

Example 2. Calculate $[OH^-]$ and pH of $0.3N$ NH_4OH solution.

Solution.

$$[OH^-] = \sqrt{K_{NH_4OH} \cdot C_{NH_4OH}} = \sqrt{1.8 \cdot 10^{-5} \cdot 3 \cdot 10^{-1}} =$$

$$= \sqrt{5.4 \cdot 10^{-6}} = 2.3 \cdot 10^{-3} \text{ g-ion/lit}$$

$$pOH = 3 - \log 2.3 = 2.64; \quad pH = 14 - 2.64 = 11.36$$

Example 3. Calculate pOH and pH of an ammonium solution containing in 1 litre 0.5 mole of NH_3 and 0.1 mole of NH_4Cl.

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[1] The hydroxides of the alkali metals (NaOH, KOH) are called caustic alkalies (or alkali hydroxides). They are the strongest bases.

Solution.

$$[OH^-] = \frac{K_{NH_4OH} \cdot C_{NH_3}}{C_{NH_4Cl}} = \frac{1.8 \cdot 10^{-5} \cdot 0.5}{0.1} = 9.0 \cdot 10^{-5} \text{ g-ion/lit}$$

$$pOH = 5 - \log 9.0 = 5 - 0.95 = 4.05; \qquad pH = 14 - 4.05 = 9.95$$

Problems

1. Calculate the hydrogen ion concentration and pH of the following solutions and present the results in a Table:

Acid	Concentration, mole/litre	Dissociation constant	$[H^+]$	pH
HCOOH	0.20	$1.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-3}$	2.22
CH_3COOH	0.01	$1.8 \cdot 10^{-5}$		
H_2S	0.02	$5.7 \cdot 10^{-8}$		
H_3PO_4	0.05	$7.6 \cdot 10^{-3}$		

2. Calculate $[H^+]$ and pH of a solution containing in 1 litre 0.06 mole of CH_3COOH and 0.02 mole of CH_3COONa ($K_{CH_3COOH} = 1.74 \cdot 10^{-5}$).

Ans. $[H^+] = 5.4 \cdot 10^{-5}$ g-ion/lit; pH = 4.27

3. Calculate the pH for each of the following solutions (a) 0.01*N* KOH; (b) 0.03*N* $Ca(OH)_2$; (c) 0.05*N* NH_4OH ($K_{NH_4OH} = 1.8 \cdot 10^{-5}$); (d) a solution containing 4 g of NaOH in 200 ml of solution.

Ans. (a) 12.0

4. Calculate the $[OH^-]$ and pH of a solution which contains 0.15 mole NH_3 and 0.03 mole of NH_4NO_3 in 1 litre of solution.

Ans. $[OH^-] = 9 \cdot 10^{-5}$; pH = 9.95

42. Buffer Solutions

Buffer solutions are those in which the hydrogen ion concentration (or pH*) does not change on dilution and changes only very slightly on adding small quantities of strong acids or alkalies.*

Buffer solutions are usually made by dissolving in water weak acids or bases and their salts. For example, the acetate buffer is a solution of acetic acid and sodium acetate; the ammonium buffer is a solution of ammonia and ammonium chloride. Sometimes a solution containing an acid salt and a neutral salt is used as a buffer solution; for example, the

carbonate buffer solution is a mixture of $NaHCO_3$ and Na_2CO_3. In this case, the first salt dissociates to form the acid HCO_3^-, while the second one is a salt of the anion of this acid.

Buffer solutions play an important role in analytical chemistry. It is often necessary to conduct precipitation at a definite pH-value. This is attained by adding the appropriate buffer solution.

Thus, a solution containing NH_4OH and NH_4Cl is used for precipitating aluminium hydroxide which partly dissolves in excess NH_4OH on using a solution containing only ammonium hydroxide. This buffer solution is also used to keep magnesium hydroxide in solution (see Sec. 62). The acetate ($CH_3COOH + CH_3COONa$) or formiate ($HCOOH + HCOONa$) buffer solution is used for precipitating zinc ions with hydrogen sulphide. Many colour reactions with organic reagents can be successfully employed only at a definite pH-value of the solution.

The hydrogen ion concentration in a solution of a weak acid and its salt is expressed by the following equation:

$$[H^+] = K_{acid} \cdot \frac{C_{acid}}{C_{salt}}$$

Hence, the concentration of hydrogen ions in such a solution depends on the dissociation constant of the acid and the ratio of the concentrations of the acid and the salt. If equal concentrations of the acid and salt are used to prepare the buffer solution, the hydrogen ion concentration will be numerically equal to the dissociation constant of the acid, as in this case the ratio $\frac{C_{acid}}{C_{salt}} = 1$. By varying the ratio of the concentrations of the acid and salt it is possible to obtain a number of solutions with various hydrogen ion concentrations, i.e., with different pH-values. An increase in the acid concentration results in an increase in the hydrogen ion concentration in the solution; an increase in the salt concentration leads to a decrease in the hydrogen ion concentration.

The addition of small quantities of acids and alkalies to a buffer solution or its dilution does not appreciably change the pH of the solution.

Problems

1. Calculate the pH- and pOH-values for buffer solutions in which the concentration of the components are equal to each other and present the results in the form of a table:

Buffer solution	$HNO_2+NO_2^-$	$HCO_3^-+CO_3^{2-}$	$HCOOH+HCOO^-$	$NH_4OH+NH_4^+$
pH	3.29	10.31		
pOH	10.71	3.62		

CHAPTER XI

Hydrolysis

43. Hydrolysis of Ions (Salts)

The aqueous solutions of many salts have an acid or alkaline reaction. As we already know, the acidity or alkalinity of an aqueous solution depends on the presence of an excess of hydrogen or hydroxyl ions in the solution; in a neutral solution the concentrations of these ions are the same and equal to 10^{-7} g-ion/lit. The presence of an excess of H^+ or OH^- ions can be explained by the reaction of ions of the salt with water. For example:

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$$
$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$$

The reaction between the ions of a salt and the hydrogen or hydroxyl ions of water is termed hydrolysis.

Let us consider four types of hydrolysis of salts.

1. Salts formed by a strong base and a weak acid. As a result of hydrolysis of such a salt, the solution contains a strongly dissociated base and a weakly dissociated acid. Hence, there are more OH^- ions than H^+ ions formed and the solution is alkaline (pH $>$ 7). For example, an aqueous sodium acetate solution is alkaline:

$$CH_3COONa + HOH \rightleftarrows NaOH + CH_3COOH$$
$$CH_3COO^- + HOH \rightleftarrows CH_3COOH + OH^-$$

In this case weakly dissociated acetic acid and strongly dissociated sodium hydroxide are formed.

2. Salts formed by a weak base and a strong acid. As a result of hydrolysis of such a salt, the solution contains a weak base and a strong acid. Hence, there are more H^+ ions than OH^- ions present in the solution and it is acidic (pH $<$ $<$ 7). For instance, an ammonium chloride solution is acidic:

$$NH_4Cl + HOH \rightleftarrows NH_4OH + HCl$$
$$NH_4^+ + HOH \rightleftarrows NH_4OH + H^+$$

In an NH_4Cl solution, weakly dissociated ammonium hydroxide, NH_4OH, and strongly dissociated hydrochloric acid, HCl, are formed.

3. Salts formed by a weak base and a weak acid. The products of hydrolysis of such salts are a weak acid and a weak base. In this case the number of H^+ or OH^- ions may predominate, depending on the degree of dissociation of the acid or base and the solution may be slightly acidic or weak-alkaline, respectively; the solution may also be neutral if the number of H^+ and OH^- ions are equal. For example, an aqueous ammonium carbonate solution is weak-alkaline:

$$(NH_4)_2CO_3 + 2HOH \rightleftarrows NH_4OH + NH_4HCO_3$$

Ammonium hydroxide is formed in the solution; the degree of dissociation of NH_4OH is greater than that of HCO_3^-.

As a result of hydrolysis, ammonium acetate forms acetic acid and ammonium hydroxide:

$$CH_3COONH_4 + HOH \rightleftarrows NH_4OH + CH_3COOH$$

The degree of dissociation of CH_3COOH and that of NH_4OH are equal; therefore, the solution is neutral.

4. Salts formed by a strong base and a strong acid. The hydrolysis of such a salt, for example, NaCl, can be expressed by the following equation:

$$NaCl + HOH \rightleftarrows NaOH + HCl$$

or

$$Na^+ + Cl^- + HOH \rightleftarrows Na^+ + OH^- + H^+ + Cl^-$$

Cancelling the ions occurring on both sides of the ionic equation, we obtain

$$H^+ + OH^- \rightleftarrows H_2O$$

From this equation it is evident that the ions of the salt do not appreciably take part in the reaction and the solution remains neutral. Thus, a salt formed by a strong base and a strong acid is not hydrolyzed and the pH of its solution is equal to 7.

For the majority of salts the process of hydrolysis is reversible. The state of hydrolytic equilibrium is characterized by the degree of hydrolysis, just as the dissociation equilibrium of a weak electrolyte is characterized by the degree of dissociation.

The degree of hydrolysis of a salt (h) is the ratio of the concentration of the hydrolyzed salt to the total concentration of the salt in the solution:

$$h = \frac{\text{number of hydrolyzed molecules of a given salt}}{\text{total number of dissolved molecules of the salt}}$$

Example. If out of every three moles of salt dissolved in water 0.015 mole is hydrolyzed, the degree of hydrolysis is equal to $\frac{0.015}{3} = 0.005$. This degree is usually expressed in per cent: $0.005 \cdot 100 = 0.5$ per cent.

Review Questions

1. To what reactions is the term *hydrolysis* applied?
2. State whether an aqueous solution of each of the following salts is acidic, alkaline or neutral: (a) KCl; (b) K_2CO_3; (c) $(NH_4)_2CO_3$; (d) $(NH_4)_2C_2O_4$.
3. What is meant by *degree of hydrolysis*?

CHAPTER XII

Oxidation-Reduction Reactions

44. General Principles

The chemical processes in which a change in the valency of the reacting elements or ions takes place are termed oxidation-reduction reactions.

The valency of an element corresponds to the number of electrons which its atoms take on or give up on reacting with other elements to form compounds. Some elements have diffe-

rent valencies in different compounds. For example, iron can be bivalent and trivalent ($FeCl_2$ and $FeCl_3$), the valency of manganese varies from 2 to 7 (MnO, Mn_2O_3, MnO_2, Mn_2O_7). Therefore, the atoms or ions of certain elements can give up or take on a different number of electrons in different reactions.

An oxidation-reduction reaction is one involving the transfer of electrons from one element or ion to another as a result of which the valency of the reacting atoms or ions is changed.

When an atom or ion is oxidized, it loses electrons whereas when it is reduced, electrons are added to it. In oxidation the positive valency of an element is increased, while the negative valency is decreased. In reduction, the positive valency of an element is decreased, while the negative valency is increased.

For example, in the conversion of sulphurous acid, H_2SO_3, to sulphuric acid, H_2SO_4, sulphur from a positive valency of four is oxidized to a positive valency of six (sulphur with a positive valency of four loses 2 electrons). When sulphurous acid is converted to hydrogen sulphide, H_2S, sulphur is reduced from a positive valency of four to a negative valency of two (sulphur with a positive valency of four takes on 6 electrons). When free sulphur is obtained from hydrogen sulphide, oxidation takes place: when the S^{2-} ion is converted to free sulphur, it loses 2 electrons and becomes electrically neutral. The conversion of $FeCl_3$ to $FeCl_2$ involves reduction of iron: Fe^{3+} takes on one electron and is converted to Fe^{2+}.

Substances containing an atom or ion capable of taking on electrons, and consequently, decreasing their positive valency or increasing their negative valency, are called oxidizing agents.

Oxidizing agents include the halogens and certain compounds containing a metal or nonmetal in the state of higher valency; for example, $KMnO_4$, HNO_3, Cl_2.

Substances containing an atom or ion capable of losing electrons, i.e., of increasing their positive valency or decreasing their negative valency are called reducing agents.

Reducing agents include metals and certain compounds containing a metal or nonmetal in the state of their lower valency; for example, $FeCl_2$, H_2S, HNO_2.

45. Oxidation-Reduction Potential

Oxidizing and reducing agents may be strong or weak. This can be made clear by the following experiment: pour into each of three different flasks 20 ml of 0.1*N* solutions of $KMnO_4$, $K_2Cr_2O_7$, $Fe_2(SO_4)_3$. To each flask add 10 ml of 2*N* H_2SO_4 solution and 5 ml of 5 per cent KI solution. Iodine is liberated in all three flasks. Hence, each of these oxidizing agents oxidizes the hydrogen iodide that is formed when potassium iodide, KI, reacts with H_2SO_4. If the test is repeated, substituting potassium bromide, KBr, for potassium iodide, and slightly heating all three flasks, free bromine will be liberated in the flasks containing $KMnO_4$ and $K_2Cr_2O_7$ (this can easily be confirmed by starch-iodide paper[1] turning blue). Bromine is not liberated in the flask containing $Fe_2(SO_4)_3$, because the latter is not capable of oxidizing hydrogen bromide. Therefore, $Fe_2(SO_4)_3$ is a weaker oxidizing agent than $KMnO_4$ and $K_2Cr_2O_7$. If sodium chloride, NaCl, is taken instead of potassium iodide or potassium bromide, chlorine will be liberated only in the flask containing the $KMnO_4$ solution, on heating it slightly.

From these examples it can be concluded that of the three oxidizing agents, $KMnO_4$, $K_2Cr_2O_7$, and $Fe_2(SO_4)_3$, the strongest oxidizing agent is $KMnO_4$; $K_2Cr_2O_7$ is weaker than $KMnO_4$ but stronger than $Fe_2(SO_4)_3$.

Reducing agents, like the oxidizing agents, may also be strong or weak. Thus, of the three reducing agents, HI, HBr, and HCl, the strongest one is HI and the weakest one is HCl.

The oxidizing properties of a substance depend on the ability of the molecules or ions to take on electrons; the reducing properties depend on the ability of giving them up.

In an oxidation-reduction process conducted under specific conditions, a given oxidizing agent is converted to a definite reducing agent; thus, the permanganate ion, MnO_4^-, in a strongly acidic solution is converted to the Mn^{2+} ion; in an alkaline solution, to MnO_2. The oxidizing agent Cl_2 is converted to the reducing agent Cl^-.

Hence, any element that is capable of exhibiting variable valency has an oxidized form (MnO_4^-, Cl_2) and a reduced

[1] Starch-iodide paper is the term for filter paper impregnated with KI solution and starch.

form (Mn^{2+}, Cl^-). In a solution containing Sn^{4+} and Sn^{2+} ions, the stannic ion, Sn^{4+}, is the oxidized form and the Sn^{2+} ion is the reduced form.

A strong oxidizing agent corresponds to a weak reducing agent; a weak oxidizing agent, to a strong reducing agent. Thus, the strong oxidizing agent Cl_2 is converted to a weak reducing agent, the Cl^- ion; the weak oxidizing agent ferric sulphate, $Fe_2(SO_4)_3$ is converted to the strong reducing agent, the Fe^{2+} ion.

The tendency to take on or to lose electrons is measured by the so-called *oxidation-reduction potential*. The greater its value, the stronger the oxidizing properties of the substance and, on the contrary, the smaller the oxidation-reduction potential, the weaker the oxidizing agent. The oxidation-reduction potential is measured electrochemically in a galvanic cell such as shown schematically in Fig. 11.

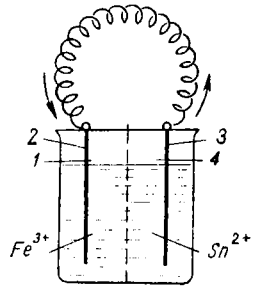


Fig. 11. Galvanic cell
1 and *4* — compartments; *2* and *3* — electrodes

The cell consists of two compartments (*1* and *4*) separated by a diaphragm that allows current to pass but keeps the solutions in the compartments from mixing. The oxidizing solution is poured on one side of the diaphragm and the reducing agent on the other side. Solid electrodes (*2* and *3*) are immersed in the solutions; platinum electrodes are usually used because they do not react with the solutions. The electrodes are connected with each other outside of the solutions by a metal wire.

If, for example, a solution of a ferric salt is poured into compartment *1*, and a solution of a stannous salt into compartment *4*, a current will be produced in the circuit because the electrons of the reducing agent Sn^{2+} will move to the ions of the oxidizing agent, Fe^{3+}. In this system, the following processes will ensue at the electrodes. At electrode *2* electrons will be added to the ferric ions:

$$Fe^{3+} + e = Fe^{2+}$$

at electrode *3*, the stannous ions will lose electrons:

$$Sn^{2+} - 2e = Sn^{4+}$$

Reduction occurs at electrode *2*; oxidation, at electrode *3*. In the galvanic cell as a whole, the following oxidation-reduction reaction takes place:

$$2Fe^{3+} + Sn^{2+} \rightleftarrows 2Fe^{2+} + Sn^{4+}$$

Electrode *2* to which the electrons move is called the positive electrode; electrode *3* from which the electrons move is called the negative electrode. The current is produced as a result of the potential difference between the electrodes: electrode *2* has a higher potential than electrode *3* and is positive with respect to the latter. The possibility that an oxidation-reduction reaction will occur and its direction is determined by the value of the potential difference.

The potentials of the electrodes vary during the reaction in the following manner. At first the positive electrode is surrounded by Fe^{3+} ions, the anions of the original salt, and molecules of water which in this case are not electrically active and do not affect the value of the electrode potential. Contact of Fe^{3+} with the electrode gives rise to the initial potential of the latter. As the oxidation-reduction reaction with stannous ions proceeds, the number of Fe^{3+} ions in the cell decreases and in their place there appear Fe^{2+} ions that have the properties of a reducing agent; as a result, the electrode potential gradually decreases.

A similar process occurs at the second electrode: the concentration of Sn^{2+} ions in its vicinity gradually decreases, whereas the concentration of Sn^{4+} ions increases; as a result, the potential of the electrode becomes more positive.

Thus, the value of the oxidation-reduction potential depends on the ratio of the concentrations of the oxidized and reduced forms in the given solution.

The value of the potential in a solution in which the concentration of the oxidized form is equal to the concentration of the reduced form is called the *standard oxidation-reduction potential.*

All potentials are usually compared with the value of the normal hydrogen electrode, the standard oxidation-reduction potential of which is taken to be equal to zero.

By comparing the values of the standard oxidation-reduction potentials of two solutions, it is possible to ascertain

the possibility and direction of the oxidation-reduction reaction that will occur on mixing these solutions.

For example, if the solution contains Fe^{3+}, Fe^{2+}, Sn^{2+}, and Sn^{4+} ions at the same time and it is necessary to decide which of the two possible reactions will occur

$$Sn^{4+} + 2Fe^{2+} \rightarrow Sn^{2+} + 2Fe^{3+}$$

or

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

it is sufficient to compare the values of the potentials of the conversion of Fe^{3+} to Fe^{2+} (0.75 V) and the conversion of Sn^{4+} to Sn^{2+} (0.15 V) to come to the conclusion that Fe^{3+} will play the role of an oxidizer with respect to Sn^{2+}. Actually, the following reaction will take place:

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

46. Writing Oxidation-Reduction Equations

To write the equation for an oxidation-reduction reaction, it is necessary to know the composition (formula) of the original substances and the reaction products obtained. On the basis of these chemical formulas it is necessary to ascertain what ions or elements have changed their valency, i.e., what substance in the given reaction is the oxidizing agent and what substance, the reducing agent.

Balancing of oxidation-reduction equations can be carried out in two ways: (a) by the method of electron balance and (b) by the ion-electron method.

Balancing by the electron method. The method of electron balance can be used when writing equations in the molecular and the ionic forms. It is recommended that the reacting substances be written in the form in which they actually take part in the reaction; for example, dissociated substances as ions and weakly dissociated substances as molecules.

To simplify balancing by the first method, it is recommended that an equation be written preliminarily in which the number of electrons taken on or given up are placed next to the ion or element that changes its valence and the symbol and valency of the ion or element obtained as a result of the addition or loss of electrons are also written. For example,

the transfer of electrons in the oxidation-reduction reaction

$$FeCl_2 + Cl_2 \rightarrow FeCl_3$$

is expressed as follows:

$$Fe^{2+} - e = Fe^{3+}$$
$$Cl_2 + 2e = 2Cl^-$$

In the course of the reaction, the Fe^{2+} ion gave up 1 electron and the Cl_2 molecule took on 2 electrons. The number of electrons given up by the reducing agent must be equal to the number of electrons added to the oxidizing agent. To find the coefficients in front of the molecules or ions of the oxidant or reductant, draw a vertical line to the left of the electronic equations and in front of this line write the multipliers required to balance the number of electrons given up and taken on in the oxidation-reduction processes:

$$\begin{array}{l|l} 2 & Fe^{2+} - e = Fe^{3+} \\ 1 & Cl_2 + 2e = 2Cl^- \end{array}$$
$$2Fe^{2+} + Cl_2^0 = 2Fe^{3+} + 2Cl^-$$

From the above electronic equations it is evident that the coefficient in front of Fe^{2+} equals 2, and that in front of Cl_2 equals 1. Hence, the following equations can be written:

$$2FeCl_2 + Cl_2 = 2FeCl_3$$
$$2Fe^{2+} + 4Cl^- + Cl_2^0 = 2Fe^{3+} + 6Cl^-$$

Let us now consider the reaction

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$$
$$\rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

On writing the skeleton equation without coefficients (showing only reactants and products) we find that Fe^{2+} and Mn^{VII} change their valency.[1] Let us write the electronic equation

$$\begin{array}{l|l} 5 & Fe^{2+} - e = Fe^{3+} \\ 1 & Mn^{VII} + 5e = Mn^{2+} \end{array}$$

Here iron is oxidized, giving away an electron to the Mn^{VII} atom; and Mn^{VII}, on being converted to Mn^{2+}, takes on 5

[1] The valency of an element that is a constituent of a complex ion or molecule is denoted by a Roman numeral.

electrons. In order that iron give up and manganese take on the required number of electrons, $5Fe^{2+}$ ions are needed for each MnO_4^- ion. Since ferric sulphate, $Fe_2(SO_4)_3$, containing $2Fe^{3+}$ ions is formed as a result of the reaction, it is necessary to take a double amount of the reducing agent and oxidizing agent, i.e., 10 molecules of $FeSO_4$ and 2 molecules of $KMnO_4$. Then the balanced electronic equation will be

$$\begin{array}{r|c|l} 10 & 5 & Fe^{2+} - e = Fe^{3+} \\ 2 & 1 & Mn^{VII} + 5e = Mn^{2+} \end{array}$$

The molecular equation and the over-all ionic equation of the reaction will be:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 =$$
$$= 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$
$$10Fe^{2+} + 2MnO_4^- + 18SO_4^{2-} + 16H^+ + 2K^+ =$$
$$= 10Fe^{3+} + 2Mn^{2+} + 2K^+ + 18SO_4^{2-} + 8H_2O$$

or cancelling what occurs on both sides we obtain

$$10Fe^{2+} + 2MnO_4^- + 16H^+ = 10Fe^{3+} + 2Mn^{2+} + 8H_2O$$

When using the electron balance method in writing the equations for oxidation-reduction reactions, proceed in the following order:

(1) ascertain the composition and formulas of the substances that react and the substances produced;

(2) determine the valency of the elements participating in the reaction in the original substances and in the products obtained;

(3) determine what substance is the oxidizing agent and what substance is the reducing agent in the given reaction and the number of electrons transferred;

(4) find the coefficients on the left-hand side of the equation by electron balance (balance with respect to electrical charges) and those on the right-hand side by atom balance (with respect to mass).

Balancing by the ion-electron method. In this method the equations for the oxidation reaction and reduction reaction are first written separately, keeping in mind that in aqueous solution, beside the oxidizing and reducing agents, H^+ and OH^- ions and H_2O molecules can also take part in the reaction.

Let us consider, for example, the reaction between aqueous solutions of $K_2Cr_2O_7$ and Na_2SO_3 in an acidic solution (for instance, in the presence of H_2SO_4):

$$K_2Cr_2O_7 + Na_2SO_3 + H_2SO_4 \rightarrow$$
$$\rightarrow K_2SO_4 + Cr_2(SO_4)_3 + Na_2SO_4 + H_2O$$

The skeleton ionic equation is

$$Cr_2O_7^{2-} + SO_3^{2-} + H^+ \rightarrow Cr^{3+} + SO_4^{2-} + H_2O$$

The scheme for the transformation of the ions of the oxidizing and reducing agents is:

(a) the $Cr_2O_7^{2-}$ ion changes to the Cr^{3+} ion;

(b) the SO_3^{2-} ion changes to the SO_4^{2-} ion.

Let us consider the conversion of $Cr_2O_7^{2-}$ to Cr^{3+}. In order that the number of atoms be the same on the left-hand and right-hand sides, it is necessary to take the oxygen away from the $Cr_2O_7^{2-}$ ion and bind its atoms in molecules of water with the aid of hydrogen ions. Since 7 atoms of oxygen must be taken, 14 hydrogen ions are needed to convert them to water:

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

After balancing the number of atoms of the elements it is necessary to balance the charges of the ions. Actually, the algebraic sum of the charges on the left-hand side is equal to plus twelve ($-2 + 14$); on the right-hand side, plus six (2×3). The charges are balanced in the system by adding to the left-hand side[1] of the equation 6 electrons: if 6 negative charges (6 electrons) are added to the 12 positive charges the sum of the charges will be 6:

$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$$

Let us now consider the oxidation reaction: $SO_3^{2-} \rightarrow SO_4^{2-}$. In order to obtain a chemically balanced equation another oxygen atom must be added to the left-hand side of the equation; this oxygen atom must be taken from a molecule of water. Then 2 hydrogen ions will appear on the right-hand side of

[1] Electrons should be added or subtracted only on the left-hand side of the equation because the oxidation-reduction reaction takes place between the original substances and both of them are on the left-hand side of the equation.

the equation

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+$$

On counting the sum of the charges we find that on the left-hand side the charge is minus two; on the right-hand, zero. Therefore, the equation is balanced with respect to charges by subtracting 2 electrons from the left-hand side of the equation.

The equation may be presented by

$$SO_3^{2-} + H_2O - 2e = SO_4^{2-} + 2H^+$$

Prior to adding the oxidation and reduction equations, each of them must be multiplied by such a number that would make the number of electrons taken on by the oxidizing agent equal to the number of electrons given up by the reducing agent:

$$\begin{array}{l|l} 1 & Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \\ 3 & SO_3^{2-} + H_2O - 2e = SO_4^{2-} + 2H^+ \end{array}$$

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ = 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

Whether the equation derived in this way is correct is checked by finding the algebraic sum of the charges on each side:

on the left-hand side: $-1 \times 2 + (-3 \times 2) + 8 \times 1 = 0$

on the right-hand side: $+2 \times 3 + (-3 \times 2) = 0$

Thus, the molecular equation will be

$$K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 =$$

$$= K_2SO_4 + Cr_2(SO_4)_3 + 3Na_2SO_4 + 4H_2O$$

Questions and Exercises

1. What reactions are called oxidation-reduction reactions?
2. How will the valency of an element change on loss or addition of electrons?
3. What is meant by *oxidizing agent*?
4. What is meant by *reducing agent*?
5. Write the molecular and ionic equations for the following reactions and point out what ions or atoms are oxidized or reduced in them: (a) $FeSO_4 + HNO_3 + H_2SO_4$; (b) $K_2Cr_2O_7 + H_2S + H_2SO_4$; (c) $Cr_2(SO_4)_3 + Cl_2 + KOH$; (d) $KMnO_4 + Na_2SO_3 + H_2SO_4$.

CHAPTER XIII

Complex Compounds

47. Complex Ions

In analytical chemistry it is often necessary to deal with double and complex salts. An example of a double salt is aluminium potassium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$; an example of a complex salt is potassium ferrocyanide $K_4[Fe(CN)_6] \cdot 3H_2O$. These salts can be obtained by combining two normal salts, for instance:

$$K_2SO_4 + Al_2(SO_4)_3 = 2KAl(SO_4)_2$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

Double salts differ from complex salts in the character of their dissociation in aqueous solutions. When double salts are dissociated, the same ions are formed as in the dissociation of the simple salts from which the double salts are obtained. Thus, K_2SO_4 and $Al_2(SO_4)_2$ dissociate according to the equations:

$$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$$
$$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$$

When the double salt $KAl(SO_4)_2$ dissociates, the same two cations, K^+ and Al^{3+}, and the anion SO_4^{2-} are formed:

$$KAl(SO_4)_2 \rightarrow K^+ + Al^{3+} + 2SO_4^{2-}$$

The simple salts KCN and $Fe(CN)_2$ from which the complex salt $K_4[Fe(CN)_6]$ is formed dissociate as follows:

$$KCN \rightarrow K^+ + CN^-$$
$$Fe(CN)_2 \rightarrow Fe^{2+} + 2CN^-$$

Dissociation of the complex salt $K_4[Fe(CN)_6]$ is expressed by the formula

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Thus, in an aqueous solution of $K_4[Fe(CN)_6]$ there are K^+ cations and $[Fe(CN)_6]^{4-}$ anions, but no Fe^{2+} and CN^- ions can be detected by the usual tests for them. This shows that Fe^{2+} and CN^- ions have combined to form the complex

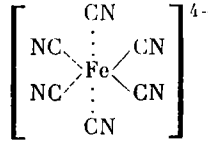
$[Fe(CN)_6]^{4-}$ ion. Ions of this type, capable of existing as crystals or in solution, are called complex ions.

Salts that on dissolving in water form complex ions are called complex salts. The composition of a complex salt is expressed by a chemical formula in which the complex ion is included in brackets. Examples are: $K_4[Fe(CN)_6]$ and $[Ag(NH_3)_2]Cl$.

The central ion which on formation of the complex attracts ions of the opposite sign or electroneutral molecules is termed a *complexing agent* (complex-forming ion). For example, in the compound $K_4[Fe(CN)_6]$ the complexing agent is Fe^{2+}; in the compound $[Ag(NH_3)_2]Cl$, it is the Ag^+ ion.

The part of the molecule of a complex salt that dissociates slightly on dissolving in water and is contained in brackets in the formula of the salt is termed the *coordination sphere* of the complex. It is said of the ions, carrying charges of a sign opposite to that of the complex ion, that they are outside the coordination sphere of the complex salt. For example, in $K_4[Fe(CN)_6]$ and in $[Ag(NH_3)_2]Cl$ the coordination spheres are $[Fe(CN)_6]^{4-}$ and $[Ag(NH_3)_2]^+$, and the K^+ and Cl^- ions are outside the coordination spheres.

The complexing ion can exhibit primary valency (normal chemical bond) and secondary or residual valency (coordinate valence bond)[1]. For example, the complexing ion Fe^{2+} in the complex ion $[Fe(CN)_6]^{4-}$ is bound to two CN^- ions by primary valency and to four CN^- ions by secondary valencies. The structure of this complex is



The ions or molecules directly bound with the central atom or ion and contained in the coordination sphere of the complex salt are called *addenda* or *ligands*.

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[1] Secondary valency, the coordinate valence bond, is denoted by dotted lines directed to the complexing ion. It is a covalent (shared) bond contributed by two electrons of one of the two atoms participating in the formation of the bond.

The number of ligands surrounding the central atom is called the *coordination number* of the given complexing atom.

Each ion has a definite maximum coordination number (2, 4, 5, 7, 8). For most metals it is equal to 6. Sometimes the coordination number of a given central atom is variable.

The valency of a complex ion is equal to the valency of the central atom if the ligands are neutral molecules, for example, NH_3, H_2O, NO. If the central atom is bound to ligands that are themselves ions: Cl^-, NO_3^-, CN^-, etc., the valency of the complex ion is equal to the difference between the valency of the central ion and the sum of the valencies of the ligand ions. In other words, the valency of the complex ion is numerically equal to the algebraic sum of the charges of the complexing ion and the ligands. Thus, in $K_4[Fe(CN)_6]$ the charge of the complexing ion, Fe^{II}, is plus two (+2), and the charge of each ligand CN^- is minus one (—1). Hence, the valency of the complex ion is equal to $2 + (-6) = -4$.

48. Instability Constant

Dissociation of a complex compound proceeds in two stages: (1) dissociation into complex and simple ions, the coordination sphere of the complex remaining intact; and (2) dissociation of the coordination sphere, resulting in decomposition of the complex. The first stage of dissociation proceeds in the same way as in the case of strong electrolytes, whereas the complex ion dissociates like a weak electrolyte. Thus, the dissociation of $[Ag(NH_3)_2]Cl$ can be presented as follows:

$$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^- \text{ (like a strong electrolyte)}$$

$$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3 \text{ (like a weak electrolyte)}$$

Dissociation of the coordination sphere of the complex, like that of any weak electrolyte, is a reversible process. In such a solution, a definite ratio is established at the moment of equilibrium between the concentration of the complex ion and the products of its dissociation (simple ions or molecules). The equilibrium constant for dissociation of the complex ion $[Ag(NH_3)_2]^+$, as that of a weak electrolyte,

can be expressed by the equation

$$K_{[Ag(NH_3)_2]^+} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

Here K is called the *dissociation constant* or *instability constant* of the complex ion. The higher the numerical value of the instability constant, the greater the degree of dissociation of the complex into the simple ions or molecules of which it is composed, and consequently, the lower its stability.

49. Effect of Complex Ion Formation on Solubility of Precipitates

In certain cases, upon adding an electrolyte with a common ion, the solubility of a precipitate does not become less but, on the contrary increases. Examples are solutions of AgCN in KCN, $Fe(CN)_2$ in KCN, etc. In these cases soluble complex salts are formed; this can be presented by the following ionic equations:

$$AgCN + CN^- = [Ag(CN)_2]^-$$
$$Fe(CN)_2 + 4CN^- = [Fe(CN)_6]^{4-}$$

Sparingly soluble salts often dissolve not only in a reagent that has a common ion but also in other solutions containing ions or molecules capable of forming a complex with the ions of the given salt. For example, the AgCl precipitate dissolves in an aqueous ammonia solution, forming a complex salt:

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl$$

If a sufficient quantity of the solvent (in the given example, aqueous ammonia solution) is added, the precipitate will be completely dissolved.

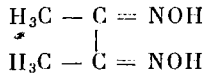
Often for detecting the presence of (identifying) a particular ion in a mixture of ions, use is made of the ability of one of them to form a stable complex. In this case the concentration of the complex-forming ion in the solution is decreased to such an extent that it does not interfere with the identification of other ions. Thus, when detecting Ni^{2+} and Co^{2+} in the presence of Fe^{3+}, the latter is bound in the complex $[FeF_6]^{3-}$ by adding KF or NaF to the solution under test. This is called *analytical masking of ions.*

50. Metallo-Organic Complex Ions. Use of Organic Reagents in Analytical Chemistry

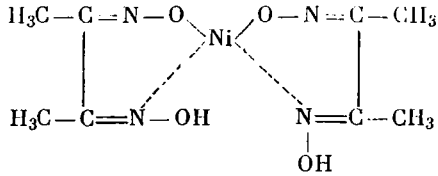
Organic reagents have a number of advantages over inorganic reagents. They possess greater ionic selectivity, i.e., under appropriate conditions they react with only one ion, although the solution may contain various other ions. Therefore, organic reagents can be used to detect ions without preliminarily isolating them. Because of the great molecular weight of organic reagents it is easy to detect the precipitate of the complex salt formed even at small concentrations of the ion under test. This is moreover possible because the complex compounds obtained are insoluble in water and they are brightly coloured.

The following organic reagents are frequently used:

Dimethylglyoxime

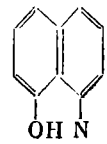


first synthesized by L. A. Chugaev and proposed by him for detecting nickel. The dimethylglyoxime molecule contains two oxime groups (= N — OH). The hydrogen in one of these groups can be replaced by a metallic ion. A coordinate bond can be formed between the nitrogen atom of the second oxime group and the metallic ion. The structural formula of the compound formed by nickel and dimethylglyoxime is

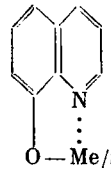


Dimethylglyoxime forms with nickel ion a bright red insoluble compound.

8-Hydroxyquinoline (oxyn)



The hydrogen in the hydroxyl group of 8-hydroxyquinoline can be replaced by a metal which, in addition, is bound coordinately with nitrogen:



8-Hydroxyquinoline forms with Al, Mg, Fe, and other ions insoluble compounds.

CHAPTER XIV

Colloidal Solutions

51. Sols and Their Coagulation

A solid on dissolving is subdivided (dispersed) into particles in the form of ions, molecules, or relatively large numbers of the same kind of molecules. In a dilute solution of the strong electrolyte NaCl, for example, there are only Na^+ and Cl^- ions present. In a solution of a nonelectrolyte (sugar) each particle is an individual molecule. Solutions in which the substance is present in the form of ions or individual molecules are called *true solutions.*

There are other solutions in which the dissolved substance is not dispersed to the molecular state, but each particle comprises a relatively large number of molecules; they are called *colloidal systems* or *sols.* Colloidal particles are larger than molecules and ions and therefore they do not penetrate (permeate) through film-membranes (animal or vegetable), whereas true solutions easily pass (diffuse) through the pores of these membranes. However, the pores of ordinary filter paper as well as other commonly used filters (glass, porcelain) are larger than colloidal particles; hence, both true and colloidal solutions easily pass through such filters.

Most of the amorphous precipitates obtained in the process of qualitative analyses readily form colloidal solutions (for example, various sulphides, the hydroxides of iron and

aluminium). The formation of colloidal solutions makes the separation of ions difficult and their occurrence therefore must be prevented.

Colloidal solutions in their properties resemble true molecular solutions of high-molecular substances with very large molecules. Such high-molecular substances include proteins, rubber, various synthetic products. On dissolving these substances, molecular dispersion is attained but the molecules, in this case, are so large that such solutions have a number of properties in common with colloidal solutions.

The stability of any solution, including a colloidal solution, is the ability of the solution to permanently retain its state, primarily its homogeneity.

In contrast to true solutions with molecular dispersion and solutions of high-molecular compounds, colloidal solutions have a limited stability. The particles in them gradually flocculate. This process is called *coagulation.*

Coagulation can be artificially accelerated by heating the colloidal solution to the boiling point or by adding an electrolyte to it. On heating the solution, the individual colloidal particles form large aggregates. The latter settle by gravity in the form of a precipitate which is easily filtered out or centrifuged. The addition of an electrolyte also accelerates coagulation of the colloid. Acids (if they do not dissolve the precipitate) or ammonium salts are used for this purpose. Acids cannot be used to coagulate the sulphides because some sulphides are dissolved by them. In this case solutions of hydrogen sulphide or ammonium salts are used.

Thus, when precipitating, filtering, centrifuging, and washing precipitates that readily assume the soluble colloidal state, suitable precautions should be taken to facilitate separation of the precipitate from the solution. Precipitation should be carried out with heating and in the presence of a suitable electrolyte. The precipitate should be filtered or centrifuged, while still hot, promptly after it is formed and it should be washed with hot water containing an electrolyte that does not dissolve the precipitate and does not interfere with the further course of analysis. The electrolyte added to the hot water is usually an ammonium salt that can be removed by ignition.

CHAPTER XV

Group III Cations

(Al^{3+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+})

52. Group Characteristics

The third analytical group includes the cations of metals of the third group of the periodic system and the cations of all the transition metals in the fourth period with the exception of copper. The ions constituting Group III cations discussed in this textbook are aluminium, chromium, ferric, ferrous, manganous, zinc, nickel, and cobalt ions.

The chemical properties of elements vary with the number of charges carried by their ions and the sign of the charges (valency). An equal charge (equal valency) explains the great resemblance between elements of different groups of the periodic system. Hence, elements in different groups of the periodic system can form similar compounds if in these compounds they exhibit the same valency. Thus, trivalent aluminium, chromium, and iron (elements of the third, sixth, and eighth groups of the periodic system) form compounds that crystallize in the same crystalline form, alums[1], similar in their solubility and reactivity.

The reagent for Group III cations is ammonium sulphide, $(NH_4)_2S$. The sulphides of the cations of this group, in contrast to the Group I and II sulphides, do not dissolve in water, but dissolve in dilute weak acids. The Group IV and V sulphides do not dissolve in water or in dilute acids.

On adding alkali hydroxides in an equivalent quantity to solutions of Group III salts, hydroxides are formed that are insoluble in water.

Aluminium, chromic, and zinc hydroxides are amphoteric, i.e., they dissolve both in acids and alkalies.

Ammonia precipitates hydroxides of the trivalent metals in the presence of ammonium salts, whereas the cations of bivalent metals are not precipitated under these conditions.

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[1] Aluminium, chromic, and ferric alums are double salts of sulphates of an alkali metal or ammonium and one of the above-named trivalent metals with the formula $MeIMeIII(SO_4)_2 \cdot 12H_2O$; for example, $KAl(SO_4)_2 \cdot 12H_2O$.

Ammonia taken in excess forms with Zn, Ni, and Co salts ammines such as $[Zn(NH_3)_4]SO_4$.

The carbonates and phosphates of Group III are not soluble in water, but dissolve in strong acids. All the carbonates and phosphates of the bivalent metals are soluble in acetic acid; ferric, chromic, and aluminium phosphates do not dissolve in acetic acid.

53. Group Reagent: Ammonium Sulphide, $(NH_4)_2S$

Ammonium sulphide, $(NH_4)_2S$, is the group reagent for Group III cations. This salt, formed by a weak base and a weak acid, is hydrolyzed according to the following equations:

$$(NH_4)_2S + HOH \rightleftarrows NH_4HS + NH_4OH$$
$$NH_4HS + HOH \rightleftarrows NH_4OH + H_2S$$

Consequently, an aqueous solution of $(NH_4)_2S$ contains NH_4^+, OH^+, HS^-, and S^{2-} ions. On adding ammonium sulphide to a solution containing Group III cations, either a sulphide or hydroxide is formed; for example: ZnS, $Al(OH)_3$, $Cr(OH)_3$.

54. Reactions of Group III Cations

It is recommended that the test results obtained on carrying out the reactions of Group III cations be tabulated in the laboratory notebook in the following form:

Reagents	Cations							
	Al^{3+}	Cr^{3+}	Fe^{3+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}
Ammonium sulphide, $(NH_4)_2S$, [action of dilute HCl on precipitate formed on adding $(NH_4)_2S$] . .								
Sodium hydroxide, NaOH, in an equivalent quantity . . .								
in excess in the cold								
in excess with heating								

Continued

Reagents	Cations							
	Al^{3+}	Cr^{3+}	Fe^{3+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}
Ammonium hydroxide, NH_4OH . . .								
Mixture of ammonium hydroxide and ammonium chloride solutions ($NH_4OH + NH_4Cl$)								
Sodium hydrogen phosphate, Na_2HPO_4								

1. Ammonium sulphide, $(NH_4)_2S$, precipitates all the Group III cations as sulphides with the exception of the aluminium and chromic ions, which are precipitated in the form of hydroxides.

The Group III sulphides differ in colour: FeS, Fe_2S_3, NiS, and CoS are black; ZnS is white; MnS is pink.

These sulphides, besides NiS and CoS, dissolve in 2*N* HCl solution; NiS and CoS dissolve in HCl only in the presence of oxidizing agents.

The following equations represent the precipitation of sulphides (or hydroxides):

(a) of the bivalent cations Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}; for example of Zn^{2+}:

$$ZnCl_2 + (NH_4)_2S = ZnS\downarrow + 2NH_4Cl$$
$$Zn^{2+} + S^{2-} = ZnS\downarrow$$

(b) of the trivalent cations; for example, of Fe^{3+}:

$$2FeCl_3 + 3(NH_4)_2S = Fe_2S_3\downarrow + 6NH_4Cl$$
$$2Fe^{3+} + 3S^{2-} = Fe_2S_3\downarrow$$

(c) of aluminium ions:

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3\downarrow + 3H_2S + 6NH_4Cl$$
$$2Al^{3+} + 6Cl^- + 6NH_4^+ + 3S^{2-} + 6H_2O =$$
$$= 2Al(OH)_3\downarrow + 3H_2S + 6NH_4^+ + 6Cl^-$$
$$2Al^{3+} + 3S^{2-} + 6HOH = 2Al(OH)_3\downarrow + 3H_2S$$

Similar reactions are characteristic of Cr^{3+} ions.

The reactions that proceed on dissolving the Group III sulphides in 2*N* HCl solution are expressed by the following equations:

(a) dissolving of a sulphide of a bivalent cation (for example, ZnS):

$$ZnS + 2HCl = ZnCl_2 + H_2S$$
$$ZnS + 2H^+ = Zn^{2+} + H_2S$$

(b) dissolving of ferric sulphide, Fe_2S_3:

$$Fe_2S_3 + 6HCl = 2FeCl_3 + 3H_2S$$
$$Fe_2S_3 + 6H^+ = 2Fe^{3+} + 3H_2S$$

The hydrogen sulphide evolved reduces the ions of the ferric salt to the ferrous salt:

$$2FeCl_3 + H_2S = 2FeCl_2 + S + 2HCl$$
$$2Fe^{3+} + H_2S = 2Fe^{2+} + S + 2H^+$$

The over-all equation for dissolving of Fe_2S_3 in acids is

$$Fe_2S_3 + 4HCl = 2FeCl_2 + 2H_2S + S$$
$$Fe_2S_3 + 4H^+ = 2Fe^{2+} + 2H_2S + S$$

(c) dissolving of nickel or cobalt sulphide in 2*N* HCl in the presence of hydrogen peroxide:

$$NiS + 2HCl + H_2O_2 = NiCl_2 + S + 2H_2O$$
$$NiS + 2H^+ + H_2O_2 = Ni^{2+} + S + 2H_2O$$

Procedure. In separate test tubes place 3-5 drops of a salt of each cation of Group III (aluminium, chromic, ferric, ferrous, manganous, zinc, nickel, and cobalt cations). To each test tube add 3-5 drops of freshly prepared $(NH_4)_2S$ solution. A precipitate of a characteristic colour is formed in each test tube: $Al(OH)_3$, white; $Cr(OH)_3$, greenish grey; FeS and Fe_2S_3, black; MnS, pink; ZnS, white; NiS and CoS, black. Centrifuge each mixture, decant the supernatant, and treat the precipitate with 2*N* HCl solution. All the precipitates dissolve in the acid except NiS and CoS.

To the insoluble precipitates of NiS and CoS add 2*N* HCl solution and 3-5 drops of 3 per cent hydrogen peroxide solution and heat the mixture. The black precipitates of nickel sulphide and cobalt sulphide will dissolve.

2. **Alkali hydroxides, NaOH and KOH,** when added in an equivalent quantity to solutions of the salts of all the Group III cations form hydroxides that are insoluble in water: $Al(OH)_3$ and $Zn(OH)_2$ white; $Cr(OH)_3$, greenish-grey; $Fe(OH)_3$, reddish-brown; $Fe(OH)_2$, white (in the air it is slowly oxidized to $Fe(OH)_3$ changing in colour from white to dirty-white, then to dark green, and finally to a dingy brown); $Mn(OH)_2$, white (in the air it is oxidized to $MnO(OH)_2$ dark brown in colour); $Ni(OH)_2$, pale green; and $Co(OH)_2$, pink (at first, on adding an insufficient quantity of alkali, a basic blue salt is precipitated, for example, Co(OH)Cl which is then converted to the pink hydroxide). All the Group III hydroxides are soluble in acids.

The equations for the formation of hydroxides of the bivalent and trivalent metals are:

$$Me^{2+} + 2OH^- = Me(OH)_2\downarrow$$
$$Me^{3+} + 3OH^- = Me(OH)_3\downarrow$$

(Me^{2+} and Me^{3+} are bivalent and trivalent cations, respectively).

The equations for oxidation of ferrous and manganous hydroxides are

(a) oxidation of ferrous hydroxide:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

(b) oxidation of manganous hydroxide:

$$4Mn(OH)_2 + O_2 + 2H_2O = 4Mn(OH)_3$$
$$4Mn(OH)_3 + O_2 = 4MnO_2 + 6H_2O$$

Procedure. Place in separate test tubes 3-5 drops of solutions of aluminium, chromic, ferric, ferrous, manganous, zinc, nickel, and cobalt salts. To each test tube add 1 or 2 drops of 2*N* NaOH or KOH solution. A precipitate appears in all the test tubes. Report the colour of each precipitate in the Table given at the beginning of the Section.

Aluminium, zinc, and chromic hydroxides are amphoteric, i.e. they dissolve both in acids and alkalies. On dissolving in alkalies, the corresponding aluminates, zincates, and chromites are formed.

When $Al(OH)_3$ dissolves in acids it reacts as follows:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$$

When $Al(OH)_3$ dissolves in alkalies, it reacts as follows:

$$Al(OH)_3 + NaOH = NaAlO_2 + H_2O$$
$$Al(OH)_3 + OH^- = AlO_2^- + 2H_2O$$

When $Cr(OH)_3$ dissolves in alkalies, it reacts in the same way.

When $Zn(OH)_2$ dissolves in alkalies, it reacts as follows:

$$Zn(OH)_2 + 2NaOH = Na_2Zn(OH)_4$$
$$Zn(OH)_2 + 2OH^- = [Zn(OH)_4]^{2-}$$

On boiling aqueous solutions containing CrO_2^-, the chromite ion is decomposed owing to hydrolysis and chromic hydroxide is reprecipitated:

$$CrO_2^- + 2H_2O \rightleftarrows Cr(OH)_3 + OH^-$$

Procedure. Place in separate test tubes 3-5 drops of solutions of an aluminium, chromic, and zinc salt. To each test tube add 2*N* NaOH or KOH solution drop by drop until the precipitate formed is dissolved. Dilute the resulting solution with 1-2 ml of water and boil for 1-2 minutes. A precipitate will appear only in the test tube containing the chromic salt.

3. Ammonium hydroxide, NH_4OH, added to a metallic salt in an equivalent amount precipitates aluminium, chromic, ferric, ferrous, manganous, and zinc hydroxides and the basic salts of nickel and cobalt. When ammonium hydroxide is taken in excess it forms with Zn^{2+}, Ni^{2+}, and Co^{2+} ions water-soluble ammines with complex ions $[Me(NH_3)_n]^{2+}$; for example, $[Zn(NH_3)_4]^{2+}$.

The precipitation of hydroxides of bivalent and trivalent metals occurs according to the following equations:

$$Me^{2+} + 2NH_4OH = Me(OH)_2\downarrow + 2NH_4^+$$
$$Me^{3+} + 3NH_4OH = Me(OH)_3\downarrow + 3NH_4^+$$

The precipitation of the basic salts of nickel and cobalt occurs in accordance with the following equations:

$$NiCl_2 + NH_4OH = Ni(OH)Cl\downarrow + NH_4Cl$$
$$Ni^{2+} + Cl^- + NH_4OH = Ni(OH)Cl\downarrow + NH_4^+$$
$$CoCl_2 + NH_4OH = Co(OH)Cl\downarrow + NH_4Cl$$
$$Co^{2+} + Cl^- + NH_4OH = Co(OH)Cl\downarrow + NH_4^+$$

Zinc hydroxide, the basic salts of nickel and cobalt, and chromic hydroxide dissolve in excess ammonium hydroxide as follows:

$$Zn(OH)_2 + 4NH_4OH = [Zn(NH_3)_4]^{2+} + 2OH^- + 4H_2O$$
$$Ni(OH)Cl + 6NH_4OH = [Ni(NH_3)_6]^{2+} + OH^- + Cl^- + 6H_2O$$
$$Co(OH)Cl + 6NH_4OH = [Co(NH_3)_6]^{2+} + OH^- + Cl^- + 6H_2O$$
$$Cr(OH)_3 + 6NH_4OH = [Cr(NH_3)_6]^{3+} + 3OH^- + 6H_2O$$

The ammines have a characteristic colour: nickel ammine is blue; cobalt ammine is yellow-brown; chromic ammine is violet in colour; zinc ammine is colourless.

The complex ion $[Co(NH_3)_6]^{2+}$ gradually turns red in the air due to oxidation of bivalent cobalt to trivalent cobalt and the formation of the complex ion $[Co(NH_3)_6]^{3+}$.

Procedure. Place in separate test tubes 3-5 drops of solutions of the salts of different cations of Group III. To each test tube add 1 or 2 drops of 2*N* ammonia solution. A small amount of ammonium hydroxide forms precipitates with all the Group III cations; the precipitates are of the same colour as those obtained with alkali hydroxides.

Add an excess of ammonia solution to the contents of each test tube. The zinc, nickel, and cobalt precipitates are dissolved. Chromic hydroxide is partially dissolved.

4. Ammonium hydroxide in the presence of ammonium salts, for example, $NH_4OH + NH_4Cl$, does not precipitate the bivalent cations but does precipitate the trivalent cations. This is explained as follows: the ammonium ion, NH_4^+, reduces the dissociation of NH_4OH to such a degree that the concentration of OH^- ions in the solution becomes less than that needed to attain the required solubility products of the hydroxides of the bivalent cations of Group III, whereas it is sufficient to attain the solubility products of the hydroxides of the trivalent cations.

Procedure. Place in separate test tubes 3 or 4 drops of solutions of salts of the different cations of Group III. To each test tube add 3 or 4 drops of 2*N* solution of NH_4Cl (or any other ammonium salt) and 2 or 3 drops of 2*N* ammonia solution. The salts of the trivalent cations precipitate the corresponding hydroxides, while no precipitate is formed in the solutions of salts of the bivalent metals.

5. **Hydrophosphates of alkali metals, Na_2HPO_4 or K_2HPO_4,** precipitate all the cations of Group III as neutral phosphates because the latter are less soluble in water than the hydrophosphates.

$AlPO_4$, $Fe_3(PO_4)_2$, $Zn_3(PO_4)_2$, and $Mn_3(PO_4)_2$ are white; $CrPO_4$ is green; $FePO_4$ is yellowish-white; $Ni_3(PO_4)_2$ is green; and $Co_3(PO_4)_2$ is violet in colour.

The equations for the precipitation of phosphates of the trivalent and bivalent cations, for example, Al^{3+} and Zn^{2+} are:

$$AlCl_3 + 2Na_2HPO_4 = AlPO_4\downarrow + NaH_2PO_4 + 3NaCl$$

$$Al^{3+} + 2HPO_4^{2-} = AlPO_4\downarrow + H_2PO_4^-$$

$$3ZnCl_2 + 4Na_2HPO_4 = Zn_3(PO_4)_2\downarrow + 2NaH_2PO_4 + 6NaCl$$

$$3Zn^{2+} + 4HPO_4^{2-} = Zn_3(PO_4)_2\downarrow + 2H_2PO_4^-$$

The phosphates of the bivalent cations of Group III, i.e., ferrous, manganous, zinc, nickel, and cobalt phosphates, are soluble in acetic acids and in mineral acids, whereas the phosphates of the trivalent cations, i.e., aluminium, chromic, and ferric phosphates, dissolve only in mineral acids; they do not dissolve in acetic acid. Aluminium, chromic, and zinc phosphates, in addition, dissolve in alkali hydroxides.

The reactions for the dissolving of aluminium phosphate in a strong acid and in an alkali hydroxide are:

$$AlPO_4 + 3HCl = AlCl_3 + H_3PO_4$$

$$AlPO_4 + 3H^+ = Al^{3+} + 3H_3PO_4$$

$$AlPO_4 + 4NaOH = NaAlO_2 + Na_3PO_4 + 2H_2O$$

$$AlPO_4 + 4OH^- = AlO_2^- + PO_4^{3-} + 2H_2O$$

Procedure. In each of several test tubes place 3 or 4 drops of a solution of salts of each cation of Group III and add to them 3 or 4 drops of $2N$ Na_2HPO_4 solution. A precipitate will appear in all the test tubes. Note the colour of each precipitate in your laboratory notebook.

Divide the precipitate of $AlPO_4$ into three parts; to one of them add hydrochloric acid, to another acetic acid, and to the third sodium hydroxide. The precipitate will dissolve in the strong acid and alkali hydroxide, whereas it will not dissolve in acetic acid.

55. Aluminium. Tests for Aluminium Ion, Al^{3+}

Aluminium is trivalent in all its compounds. It forms only one oxide, Al_2O_3, which is amphoteric, i.e., dissolves both in acids and in alkalies. Compounds containing Al^{3+} ions are colourless.

1. Alkalies, taken in excess, form with aluminium salts aluminates of alkali metals (see Sec. 54, *P* 2). Aluminates being salts of weak acids are hydrolyzed as follows:

$$AlO_2^- + 2H_2O = Al(OH)_3 + OH^-$$

To shift the equilibrium to the right it is necessary to reduce the concentration of OH^- ions. This is achieved, for example, by introducing a dry ammonium salt or its concentrated solution into the solution of the aluminate of an alkali metal.

The equations for the reaction between the aluminate and the ammonium salt are:

$$NaAlO_2 + NH_4Cl + 2H_2O = Al(OH)_3 + NH_4OH + NaCl$$

$$AlO_2^- + NH_4^+ + 2H_2O = Al(OH)_3 + NH_4OH$$

Cr^{3+} ions react with alkalies the same way as aluminium ions and, therefore, they interfere with the test for Al^{3+}.

Procedure. To a few drops of the solution under test add 2*N* NaOH solution until the reaction to litmus is strongly alkaline. Centrifuge if a precipitate appears. Add solid NH_4Cl in small portions to the supernatant and boil the mixture until no NH_3 is evolved after adding a new portion of NH_4Cl. In the presence of aluminium, a white precipitate will appear.

2. Alizarin-S reagent with Al^{3+} ions forms a red complex salt that is insoluble in acetic acid. The reaction with Alizarin-S reagent should be carried out in a slightly acidic solution at a pH = 4.2-4.6. Fe^{3+} ion interferes with the test because it also forms a coloured precipitate.

Procedure. To a few drops of the solution under test add 2*N* NaOH solution until the reaction to litmus is strongly alkaline. If a precipitate appears, centrifuge the mixture, discard the precipitate, and add to the supernatant 1 or 2 drops of 0.2 per cent Alizarin-S reagent. The liquid will assume a violet colour. Add 2*N* CH_3COOH solution to it a

drop at a time until the solution is acidic. In the presence of aluminium ions, depending on the concentration, either a red precipitate will form or the solution will turn red.

56. Chromium. Tests for Chromic Ion, Cr^{3+}; Chromate Ion, CrO_4^{2-}; Dichromate Ion, $Cr_2O_7^{2-}$

Chromium can be present in its compounds in the form of ions of different valencies: as the chromous and chromic cations, Cr^{2+} and Cr^{3+}; and as the chromate and dichromate anions, CrO_4^{2-} and $Cr_2O_7^{2-}$, in which chromium is hexavalent.

Chromous salts (of a blue or red colour) are readily oxidized by atmospheric oxygen to chromic compounds (of a green colour). Salts containing Cr^{3+} can be further oxidized to compounds of hexavalent chromium.

The dichromate ion in an acidic solution is a strong oxidizing agent. In an alkaline solution it is converted to the chromate ion which is a weak oxidizing agent.

Chromic salts can be oxidized to dichromates by strong oxidizing agents in an acidic solution. Such oxidizing agents are the persulphate ion, $S_2O_8^{2-}$, and the permanganate ion, MnO_4^-. Weaker oxidizing agents such as chlorine, bromine, hydrogen peroxide can be used to oxidize chromic ions (i.e., $Cr(OH)_3$ or CrO_2^-) in an alkaline medium. The process of oxidation of trivalent chromium to compounds in which chromium is hexavalent is accompanied by a change in colour of the solution from green or blue-violet, characteristic of solutions containing trivalent chromium, to yellow (colour of CrO_4^{2-}) or red-orange (colour of $Cr_2O_7^{2-}$). Consequently, the reaction of oxidation of trivalent chromium to hexavalent chromium can serve as a test for chromic ions.

Various methods of converting trivalent chromium to hexavalent chromium are described below (*P* 1 to *P* 3).

1. Oxidation of the chromic cation with hydrogen peroxide or sodium peroxide.

$$2Cr(OH)_3 + 3H_2O_2 + 4NaOH = 2Na_2CrO_4 + 8H_2O$$

$$\begin{array}{r|l} 2 & Cr(OH)_3 + 5OH^- - 3e = CrO_4^{2-} + 4H_2O \\ 3 & H_2O_2 + 2H^+ + 2e = 2H_2O \end{array}$$

$$2Cr(OH)_3 + 3H_2O_2 + 4OH^- = 2CrO_4^{2-} + 8H_2O$$

Procedure. To 3-5 drops of the solution under test placed in an evaporating dish add 3-5 drops of 2*N* alkali solution and 3-5 drops of 3 per cent hydrogen peroxide solution (or a small crystal of sodium peroxide instead of H_2O_2). Boil the solution until oxygen bubbles are no longer evolved. In the presence of chromium the solution will assume a yellow colour.

2. Oxidation of the chromic cation with ammonium persulphate in an acidic solution to $Cr_2O_7^{2-}$. Oxidation with ammonium persulphate, $(NH_4)_2S_2O_8$, or potassium persulphate, $K_2S_2O_8$, in a nitric acid solution in the presence of silver nitrate proceeds as follows:

$$Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 7H_2O =$$
$$= H_2Cr_2O_7 + 3(NH_4)_2SO_4 + 6H_2SO_4$$

$$\left.\begin{array}{l} 1 \\ 3 \end{array}\right| \begin{array}{l} 2Cr^{3+} + 7H_2O - 6e = Cr_2O_7^{2-} + 14H^+ \\ S_2O_8^{2-} + 2e = 2SO_4^{2-} \end{array}$$

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O = Cr_2O_7^{2-} + 6SO_4^{2-} + 14H^+$$

In this reaction the Ag^+ ion acts as a catalyzer. The persulphate first reacts with Ag^+ to convert it to the peroxide, Ag_2O_2:

$$2Ag^+ + S_2O_8^{2-} + 2H_2O = Ag_2O_2 + 2SO_4^{2-} + 4H^+$$

Bivalent silver oxidizes the Cr^{3+} ion to the $Cr_2O_7^{2-}$ ion in an acidic solution.

Procedure. Place in a test tube 3-5 drops of 2*N* HNO_3 solution, 2 or 3 drops of 0.1*N* $AgNO_3$ solution, 3-5 drops of the solution under test and 5-8 drops of 50 per cent $(NH_4)_2S_2O_8$ solution or a tiny crystal of $(NH_4)_2S_2O_8$. Heat the mixture almost to the boiling point. In the presence of chromium the solution will assume an orange colour.

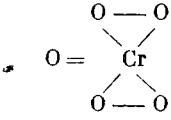
3. Oxidation of the chromic ion to chromium peroxide. After oxidizing trivalent chromium to hexavalent chromium, an additional reaction can be carried out to oxidize hexavalent chromium to CrO_5 which has a blue colour. First oxidize trivalent chromium to hexavalent chromium with hydrogen peroxide or sodium peroxide. If a precipitate appears, centrifuge and discard the precipitate. Then test for hexavalent chromium in the supernatant (see *P* 4).

Trivalent chromium can be oxidized to hexavalent chromium in another way: place in a test tube 5 drops of 0.1*N*

$AgNO_3$ solution and $2N$ HNO_3 solution, add a tiny crystal of $(NH_4)_2S_2O_8$ or $K_2S_2O_8$ and a few drops of the solution under test. Heat the mixture almost to the boiling point and then cool. In another test tube mix 3-5 drops of $2N$ H_2SO_4 solution, 5-8 drops of 3 per cent hydrogen peroxide solution and 5-8 drops of ether. To this mixture add a few drops of the cold clear solution previously obtained and shake vigorously. In the presence of chromium the ether layer will assume a blue colour.

4. Oxidation of hexavalent chromium cations with hydrogen peroxide in an acidic solution to CrO_5. Hexavalent chromium can also be identified by oxidation to CrO_5. Thus, this is a test for both trivalent and hexavalent chromium.

The structural formula of chromium peroxide, CrO_5, is



Hydrogen peroxide in an acidic solution converts the $Cr_2O_7^{2-}$ ion to chromium peroxide, CrO_5, which is blue in colour.

The reaction that takes place is

$$Na_2Cr_2O_7 + 4H_2O_2 + 2HNO_3 = 2CrO_5 + 2NaNO_3 + 5H_2O$$

$$\begin{array}{r|l} 1 & Cr_2O_7^{2-} + 3H_2O - 8e = 2CrO_5 + 6H^+ \\ 4 & H_2O_2 + 2H^+ + 2e = 2H_2O \end{array}$$

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ = 2CrO_5 + 5H_2O$$

On dissolving in water, chromium peroxide forms perchromic acid, H_2CrO_6 (its exact structural formula has not as yet been ascertained). Perchromic acid and its salts are blue in colour. The salts as well as the acid itself is stable in ether solution and imparts a blue colour to it. In aqueous solutions these compounds decompose in an alkaline solution to form yellow chromate ions; in an acidic solution to form green chromic ions:

$$\left.\begin{array}{l} CrO_5 + 2NaOH = Na_2CrO_4 + O_2 + H_2O \\ CrO_5 + 2OH^- = CrO_4^{2-} + O_2 + H_2O \end{array}\right\} \text{in an alkaline solution}$$

$$\left.\begin{array}{l} 4CrO_5 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 7O_2 + 6H_2O \\ 4CrO_5 + 12H^+ = 4Cr^{3+} + 7O_2 + 6H_2O \end{array}\right\} \text{in an acidic solution}$$

Procedure. In a test tube mix 5-8 drops of 3 per cent hydrogen peroxide solution, 3-5 drops of $2N$ H_2SO_4 solution, and 5-8 drops of ether. To the mixture add 3-5 drops of the solution under test and immediately shake it vigorously. Then allow it to stand. In the presence of chromates or dichromates the ether layer will turn blue.

57. Iron. Tests for Ferrous Ion, Fe^{2+}, and Ferric Ion, Fe^{3+}

Iron in its compounds can be bivalent (Fe^{2+}, the ferrous ion), trivalent (Fe^{3+}, the ferric ion), and hexavalent (FeO_4^{2-}, the ferrate ion).

1. Potassium ferrocyanide, $K_4[Fe(CN)_6]$, precipitates Fe^{3+} ions as ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, of a dark blue colour (Prussian blue):

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3\downarrow + 12KCl$$

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]_3\downarrow$$

The precipitate of $Fe_4[Fe(CN)_6]_3$ does not dissolve in acids but is decomposed by alkalies to form ferric hydroxide and the ferrocyanide of the alkali metal:

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 4Fe(OH)_3 + 3K_4[Fe(CN)_6]$$

$$Fe_4[Fe(CN)_6]_3 + 12OH^- = 4Fe(OH)_3 + 3[Fe(CN)_6]^{4-}$$

Procedure. To 2 or 3 drops of the solution under test add 1 or 2 drops of $2N$ HCl solution and 1 or 2 drops of $K_4[Fe(CN)_6]$. In the presence of ferric ions a dark blue precipitate will appear.

2. Potassium thiocyanate, KSCN, or ammonium thiocyanate, NH_4SCN, react with ferric ions to form blood-red ferric thiocyanate:

$$Fe^{3+} + 3SCN^- = Fe(SCN)_3$$

Procedure. Place 1 or 2 drops of the solution under test in a test tube, add 1 or 2 drops of $2N$ HCl solution and 3 or 4 drops of potassium or ammonium thiocyanate. In the presence of ferric ions the solution will turn blood red.

3. Acetates of alkali metals, $NaC_2H_3O_2$ and $KC_2H_3O_2$, and ammonium acetate, $NH_4C_2H_3O_2$, form, in the cold, with the Fe^{3+} ion a red precipitate, $Fe(C_2H_3O_2)_3$, which is hydro-

lyzed, especially if diluted with water (gradually in the cold, more rapidly on heating). At first the solution changes in colour and then a reddish-brown precipitate of the basic ferric acetate, $Fe(OH)_2(CH_3COO)$, appears:

$$FeCl_3 + 3CH_3COONa = Fe(CH_3COO)_3 + 3NaCl$$

$$Fe^{3+} + 3CH_3COO^- \rightleftharpoons Fe(CH_3COO)_3$$

$$Fe(CH_3COO)_3 + 2H_2O = Fe(OH)_2(CH_3COO) + 2CH_3COOH$$

Procedure. To 3-5 drops of the solution under test add 8-10 drops of 2*N* solution of an acetate of an alkali metal or ammonium. The solution will turn dark red in the cold if Fe^{3+} ions are present. On boiling for 2-3 minutes, a reddish-brown precipitate will appear.

4. Potassium ferricyanide, $K_3[Fe(CN)_6]$, forms with ferrous ions a dark blue precipitate of $Fe_3[Fe(CN)_6]_2$, Turnbull's blue:

$$3FeSO_4 + 2K_3[Fe(CN)_6] = Fe_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4$$

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} = Fe_3[Fe(CN)_6]_2\downarrow$$

The precipitate of $Fe_3[Fe(CN)_6]_2$ does not dissolve in acids and is decomposed by the alkali hydroxides to form ferrous hydroxide:

$$Fe_3[Fe(CN)_6]_2 + 6KOH = 3Fe(OH)_2 + 2K_3[Fe(CN)_6]$$

$$Fe_3[Fe(CN)_6]_2 + 6OH^- = 3Fe(OH)_2 + 2[Fe(CN)_6]^{3-}$$

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of 2*N* HCl solution and 2 or 3 drops of $K_3[Fe(CN)_6]$. The immediate formation of a dark blue precipitate confirms the presence of Fe^{2+} ions.

58. Manganese. Tests for Manganous Ion, Mn^{2+}

Manganese forms bivalent, trivalent, tetravalent, hexavalent, and heptavalent ions. We will consider only manganous compounds, i.e., compounds containing Mn^{2+} ions. Salts of trivalent and tetravalent manganese are unstable and are easily decomposed. Hexavalent and heptavalent manganese do not form cations but are constituents of anions.

The manganous ion is relatively readily oxidized to the MnO_4^- ion by strong oxidizing agents in an acidic solution. The oxidation of Mn^{2+} ions is accompanied by a characteri-

stic change in colour of the solution: the almost colourless solution of a manganous salt turns purple when Mn^{2+} ions are oxidized to MnO_4^-. Thus, oxidizing agents capable of converting the Mn^{2+} ion to the MnO_4^- ion are characteristic reagents for identifying the Mn^{2+} ion. Such oxidizing agents are sodium bismuthate, $NaBiO_3$, ammonium persulphate, $(NH_4)_2S_2O_8$, lead dioxide, PbO_2, or red lead, Pb_3O_4.

Chlorides, bromides, and iodides interfere with the test for Mn^{2+} because Cl^-, Br^-, and I^- ions are oxidized by the permanganate ion and the solution is decolourized.

1. Sodium bismuthate, $NaBiO_3$, in nitric acid solution in the cold oxidizes the Mn^{2+} ion to MnO_4^-:

$$2MnSO_4 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + 2Na_2SO_4 + NaNO_3 + 7H_2O$$

$$2 \mid Mn^{2+} + 4H_2O - 5e = MnO_4^- + 8H^+$$

$$5 \mid BiO_3^- + 6H^+ + 2e = Bi^{3+} + 3H_2O$$

$$2Mn^{2+} + 5BiO_3^- + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

Procedure. Place a pinch of $NaBiO_3$ in a test tube, add 3 or 4 drops of HNO_3 (sp gr 1.2), 3 or 4 drops of 0.1*N* $AgNO_3$ solution, and 1 or 2 drops of the solution under test. Stir the mixture with a glass rod and allow to stand. In the presence of Mn^{2+} the supernatant liquid will turn purple. The test can be conducted on a spot plate.

2. Ammonium persulphate, $(NH_4)_2S_2O_8$, in the presence of a catalyzer ($AgNO_3$) oxidizes the Mn^{2+} ion to MnO_4^- and the solution assumes a purple colour:

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O = 2HMnO_4 + 5(NH_4)_2SO_4 + 7H_2SO_4$$

$$2 \mid Mn^{2+} + 4H_2O - 5e = MnO_4^- + 8H^+$$

$$5 \mid S_2O_8^{2-} + 2e = 2SO_4^{2-}$$

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O = 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

When the concentration of Mn^{2+} is low the solution is pink; in the presence of excess Mn^{2+} it becomes brown due to the formation of MnO_2.

Procedure. Take 2 or 3 tiny $(NH_4)_2S_2O_8$ crystals, add 5-8 drops of 2*N* HNO_3 solution and 2 or 3 drops of 0.1*N* $AgNO_3$ solution. Heat the mixture almost to the boiling point, but do not boil. Immerse in the hot solution a stirring rod pre-

viously wetted with the solution under test and heat to approximately 50°C for 1-2 minutes. In the presence of manganese the solution assumes a purple colour.

3. Lead dioxide, PbO_2, or red lead, Pb_3O_4, in nitric acid solution oxidizes the Mn^{2+} ion to MnO_4^-:

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + \\ + 3Pb(NO_3)_2 + 2H_2O$$

$$\begin{array}{r|l} 2 & Mn^{2+} + 4H_2O - 5e = MnO_4^- + 8H^+ \\ 5 & PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O \end{array}$$

$$2Mn^{2+} + 5PbO_2 + 6H^+ = 2HMnO_4 + 5Pb^{2+} + 2H_2O$$

The equation for the reaction when red lead is used for oxidation is

$$2MnSO_4 + 5Pb_3O_4 + 26HNO_3 = \\ = 2HMnO_4 + 2PbSO_4 + 13Pb(NO_3)_2 + 12H_2O$$

$$\begin{array}{r|l} 2 & Mn^{2+} + 4H_2O - 5e = MnO_4^- + 8H^+ \\ 5 & Pb_3O_4 + 8H^+ + 2e = 3Pb^{2+} + 4H_2O \end{array}$$

$$2Mn^{2+} + 5Pb_3O_4 + 24H^+ = 2MnO_4^- + 15Pb^{2+} + 12H_2O$$

Procedure. Place a pinch of PbO_2 or Pb_3O_4 in a test tube, add 1 ml of concentrated HNO_3 and 3-5 drops of 0.1*N* $AgNO_3$ solution. Stir the mixture with a stirring rod and boil for 1-2 minutes. Add to the test tube not more than 1 or 2 drops of the solution under test and reheat the mixture to boiling.

After cooling, add 3-5 drops of water and centrifuge. In the presence of manganese the liquid above the precipitate will be coloured purple.

59. Zinc. Test for Zinc Ion, Zn^{2+}

Zinc is always bivalent in its compounds. It forms zinc oxide, ZnO, zinc hydroxide, $Zn(OH)_2$; both compounds are white in colour and amphoteric.

Hydrogen sulphide precipitates Zn^{2+} as ZnS which is also white:

$$Zn^{2+} + H_2S \rightleftarrows ZnS + 2H^+$$

ZnS is precipitated at pH = 2.5; the other cations of Group III are not precipitated in such conditions.

The precipitation of Zn^{2+} with hydrogen sulphide from solutions of salts of inorganic acids cannot be quantitative

because of the accumulation of H^+ ions that shift the reaction in the direction of dissolving of ZnS. Complete precipitation of zinc ions as zinc sulphide is achieved only on adding an acetate of an alkali metal. In this case, the hydrogen ions form with the acetate ions acetic acid, CH_3COOH, which is slightly dissociated; hence, the concentration of H^+ ions is lowered and ZnS stops dissolving:

$$ZnSO_4 + H_2S + 2CH_3COONa = ZnS + 2CH_3COOH + Na_2SO_4$$
$$Zn^{2+} + H_2S + 2CH_3COO^- = ZnS + 2CH_3COOH$$

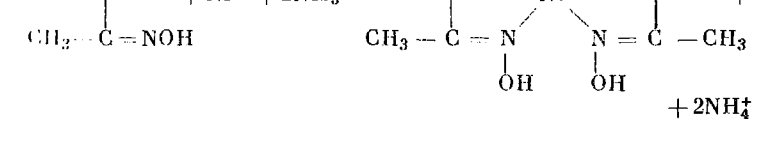
The most suitable medium for precipitating zinc sulphide is one with a pH from 2 to 3. In solutions that are more acidic, precipitation is incomplete; while in those that are more alkaline, a slimy precipitate is formed that is difficult to filtrate. The required hydrogen ion concentration can be achieved by adding a buffer solution consisting of a mixture of formic acid and ammonium formiate. The sulphides of the other cations of Group III are not precipitated at a pH from 2 to 3. Thus, at this hydrogen ion concentration, hydrogen sulphide is an identification reagent for the zinc ion.

Procedure. To 5-8 drops of the solution under test add an equal volume of the formiate buffer solution prepared from $2N$ formic acid solution and $2N$ sodium formiate solution taken in a ratio of 1 : 1 by volume and pass H_2S through the mixture. ZnS will be formed in the presence of zinc.

60. Nickel. Test for Nickel Ion, Ni^{2+}

Nickel forms compounds in which it is bivalent, trivalent, or tetravalent. We will consider compounds of Ni^{2+}. The only known compounds of trivalent and tetravalent nickel are Ni_2O_3 and NiO_2 which are strong oxidizing agents.

Dimethylglyoxime (Chugayev's reagent) in an ammoniacal solution forms with nickel a bright red precipitate of nickel dimethylglyoxime, a complex salt:



The compound formed is soluble in acids and alkalies but is insoluble in dilute ammonia solutions. The cations of elements that form insoluble hydroxides interfere with this test. The effect of Fe^{3+} ions can be eliminated by binding them in stable complex ions of fluorides of the alkali metals. Fe^{2+} ions are preliminarily oxidized to Fe^{3+} with H_2O_2 and then the Fe^{3+} ions are bound in a complex with the fluoride of an alkali metal.

Procedure. In a test tube mix 1 or 2 drops of the solution under test and 1 or 2 drops of 1 per cent alcoholic solution of dimethylglyoxime and add ammonia solution until the mixture is weak-alkaline. The appearance of a bright red precipitate indicates the presence of Ni^{2+}. If ferric ions are present in the solution under test, a small amount of solid NaF is preliminarily added to it.

61. Cobalt. Tests for Cobalt Ion, Co^{2+}

Cobalt forms compounds in which it is bivalent, trivalent, and tetravalent.

1. Ammonium or potassium thiocyanate forms with Co^{2+} salts the complex ion $[Co(SCN)_4]^{2-}$ of a blue colour. It is stable in a solution containing 50 per cent of acetone or in a mixture of amyl alcohol and ether. In aqueous solutions the complex ion $[Co(SCN)_4]^{2-}$ dissociates into Co^{2+} and SCN^- ions.

The presence of Fe^{3+} ions interferes with this test because it forms the red complex ion $[FeSCN]^{2+}$ which is also extracted by the ether solution of amyl alcohol or by acetone and the blue colour disappears. Therefore, to the solution containing Co^{2+} and Fe^{3+} ions it is necessary to add a fluoride of an alkali metal, which forms a complex salt with ferric ions. In this case the iron does not produce a red colour with SCN^- and does not interfere with the test for cobalt ions.

Procedure. To 2 or 3 drops of the solution under test add 1 or 2 crystals of the dry salt or 3-5 drops of a saturated aqueous solution of NH_4SCN or KSCN, 1 or 2 tiny NaF crystals, 3-5 drops of amyl alcohol and 3-5 drops of ethyl ether. Shake the resulting mixture vigorously and let stand. The ether-alcohol layer turns blue in the presence of cobalt.

The test can be carried out in another way: to 2 or 3 drops of the solution under test add 1 or 2 small NaF crystals and 1 ml of a saturated solution of NH_4SCN or KSCN in acetone. In the presence of cobalt the liquid will assume a blue colour.

2. Ammonium mercuri-thiocyanate, $(NH_4)_2$ [$Hg(SCN)_4$], (prepared as described in Appendix 3B) forms with Co^{2+} ions in the presence of Zn^{2+} ions a blue precipitate, $Co[Hg(SCN)_4]\cdot Zn[Hg(SCN)_4]$:

$$CoSO_4 + ZnSO_4 + 2(NH_4)_2[Hg(SCN)_4] =$$
$$= Co[Hg(SCN)_4]\cdot Zn[Hg(SCN)_4]\downarrow + 2(NH_4)_2SO_4$$
$$Co^{2+} + Zn^{2+} + 2[Hg(SCN)_4]^{2-} =$$
$$= Co[Hg(SCN)_4]\cdot Zn[Hg(SCN)_4]\downarrow$$

Procedure. To 1 or 2 drops of the slightly acidic solution under test add 1 or 2 drops of a zinc salt and 3-5 drops of $(NH_4)_2[Hg(SCN)_4]$. Shake the mixture and rub a glass rod against the inner wall of the test tube. A blue precipitate will be formed in the presence of cobalt.

62. Systematic Analysis of Mixture of Cations of Groups I, II, and III in the Absence of Phosphate Ions

All the cations of Group III are precipitated by the sulphide ion in an ammoniacal solution (at pH > 7) as water-insoluble sulphides or hydroxides and are thus separated from the cations of Groups I and II. To avoid precipitation of magnesium hydroxide on adding the ammonia solution and ammonium sulphide, it is necessary to previously introduce ammonium chloride in such a quantity that the concentration of NH_4^+ ions in the solution approximately equals 1.0 g-ion per litre.

The presence of ammonium chloride is necessary for the precipitation of Group III cations not only to keep the magnesium ions in the solution but also to decrease the solubility of $Al(OH)_3$ and $Cr(OH)_3$ (due to their amphoteric character they dissolve partially in NH_4OH) and also to coagulate the Group III sulphides and hydroxides.

Since the character of the precipitate is of great significance for successful filtering or centrifuging, it is essential that precipitation of Group III cations be carried out under

strictly specified conditions. To obtain sulphides that are readily filtered, one of the following procedures should be followed: (a) pass hydrogen sulphide into an acidic solution and then add ammonia solution until the solution is just alkaline; (b) pass hydrogen sulphide into an alkaline solution; (c) precipitate with ammonium sulphide. In all cases avoid an excess of ammonia because in its presence the precipitate passes through the pores of the filter.

When precipitating Group III cations with hydrogen sulphide in an acidic solution proceed as follows. Acidify the solution under test with 2*N* hydrochloric acid solution, heat to boiling and slowly pass hydrogen sulphide into the hot solution. Then add 2*N* ammonia solution drop by drop until the reaction is alkaline to litmus. Heat again to boiling and pass hydrogen sulphide once more into the hot solution. Allow the precipitate formed to settle and add 1 or 2 drops of 2*N* NH_4OH solution. Heat the mixture to boiling and, stirring constantly, boil for 1-2 minutes. Then centrifuge or filter the mixture and test for completeness of precipitation.

When precipitating with hydrogen sulphide in an alkaline solution, add NH_4Cl to the solution under test and then 2*N* NH_4OH solution drop by drop until the solution is just alkaline. Heat the mixture to boiling and pass hydrogen sulphide into the hot solution.

It is somewhat simpler to precipitate with a freshly prepared ammonium sulphide solution. The reaction is carried out as follows. To the solution under test add 2-3 ml of 2*N* NH_4Cl solution and 2*N* NH_4OH solution drop by drop until the solution is weak-alkaline. Heat the mixture to boiling and then add the freshly prepared ammonium sulphide solution a drop at a time, with thorough stirring between successive additions, until no more precipitate forms. Heat the mixture to boiling once more, boil for 1-2 minutes, centrifuge, check for completeness of precipitation, and separate the solution from the precipitate.

Hydrogen sulphide in an alkaline solution or ammonium sulphide precipitates iron, manganese, zinc, nickel, and cobalt as sulphides, and aluminium and chromium as hydroxides. Dissolve the Group III sulphides and hydroxides in nitric acid (sp gr 1.2) in the presence of a small quantity of KNO_2 or $NaNO_2$.

The procedure for analyzing the mixture of Group III cations is described below.

When analyzing a mixture of cations of Groups I, II, and III in the absence of phosphate ions, first of all note the colour of the solution under test, because the presence or absence of certain ions can often be ascertained approximately by the colour. A green colour indicates the presence of Cr^{3+} or Ni^{2+} ions; a greenish colour, that of Fe^{2+}; a yellowish colour, that of Fe^{3+}; pink, the presence of Co^{2+}. However, if the solution contains several coloured ions it is impossible to ascertain for certain the presence of a particular ion. For example, Ni^{2+} and Co^{2+} may be present in such a ratio that the solution is nearly colourless.

The analysis of mixtures of cations of Groups I, II, and III is carried out in the following order:

1. Test for Group III cations. Add 2-5 drops of $2N$ NH_4Cl solution and $2N$ NH_4OH solution to 3-5 drops of the solution under test until it is alkaline. Heat the mixture to boiling. Add 3-5 drops of $(NH_4)_2S$ or pass hydrogen sulphide into the solution[1]. The appearance of a precipitate indicates the presence of Group III cations.

2. Preliminary tests. NH_4^+, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+} ions can be preliminarily detected in separate portions of the solution under test.

Test for ferrous ion, Fe^{2+}. This test should be carried out first of all because Fe^{2+} ions are readily oxidized by oxygen of the air to Fe^{3+} and it becomes difficult to detect Fe^{2+} in solutions that are allowed to stand for a long period of time.

Place 2 or 3 drops of the solution under test in a test tube, add 2 or 3 drops of $2N$ HCl solution and a drop of $K_3[Fe(CN)_6]$ solution. In the presence of Fe^{2+} ions a blue precipitate will appear. If a precipitate of some other colour appears, the presence of Fe^{2+} is not indicated.

Tests for ferric ion, Fe^{3+}. Carry out one of the following tests:

(a) to 2 or 3 drops of the solution under test placed on a spot plate or in a test tube add 1 or 2 drops of $2N$ HCl so-

[1] Ammonium polysulphide, $(NH_4)_2S_n$, solution cannot be used because it contains S_2^{2-}, S_3^{2-}, etc., ions but does not contain S^{2-} ions.

lution and a drop of $K_4[Fe(CN)_6]$ solution. The formation of a blue precipitate indicates the presence of Fe^{3+} ions. If there are only traces of iron, the solution will turn blue.

(b) place a drop of the solution under test on filter paper or in a test tube and add a drop of KSCN or NH_4SCN solution. The appearance of an intense red colour confirms the presence of Fe^{3+}. A weak red colour shows that only traces of iron are present.

Tests for manganous ion, Mn^{2+}. Place in a test tube a pinch of $NaBiO_3$, 3 or 4 drops of HNO_3 solution (sp gr 1.2) and 1 or 2 drops of the solution under test. Stir the mixture with a glass rod and allow to stand for 1-2 minutes. In the presence of manganese the liquid above the precipitate will turn purple.

Mn^{2+} ions can also be detected with ammonium persulphate (see Sec. 58, *P* 2).

Test for chromic ion, Cr^{3+}. Place 8-10 drops of the solution under test in a small evaporating dish or crucible, add 8-10 drops of 2*N* alkali solution and 5-8 drops of hydrogen peroxide. Boil the solution until oxygen bubbles are no longer liberated. Centrifuge the mixture and separate the precipitate from the supernatant. In another test tube mix 5 or 6 drops of 2*N* H_2SO_4 solution, 8-10 drops of 3 per cent hydrogen peroxide solution, and 5 or 6 drops of ether. Add to this mixture 3 or 4 drops of the supernatant obtained and shake the test tube vigorously. If the ether layer assumes a blue colour, chromic ions are present. Sometimes the ether layer fails to change colour, but at the moment when the previously cooled supernatant is added to the mixture of H_2SO_4, H_2O_2, and ether, the aqueous layer turns a blue colour that quickly disappears. The appearance of the unstable blue coloration of the aqueous layer also confirms the presence of chromium.

Test for ammonium ion, NH_4^+. To 5 or 6 drops of the solution under test add 2*N* NaOH or KOH solution until the hydroxides are completely precipitated. Centrifuge the mixture, pour the clear liquid into another test tube and add to it 3-5 drops of Nessler's reagent. The appearance of a red-brown precipitate or coloration of the solution confirms the presence of NH_4^+ ions.

3. Separation of Group III cations from cations of Groups I and II. To 5-8 ml of the solution under test add 2*N* HCl

solution until the solution is acidic to litmus. Heat the mixture to boiling. Pass hydrogen sulphide slowly into the hot solution for 2-3 minutes. Then slowly add 2*N* NH_4OH solution drop by drop until the solution is alkaline. Heat the mixture once more to boiling and again pass H_2S in. Allow the precipitate to settle and add 1 or 2 drops of 2*N* NH_4OH solution into the test tube. To obtain a more compact precipitate, heat the mixture, stirring constantly with a glass rod, and boil for 1-2 minutes. Centrifuge. Check for completeness of precipitation as follows. Without separating the precipitate from the solution add 1 or 2 drops of $(NH_4)_2S$ solution to the supernatant liquid or pass H_2S into it. The liquid over the precipitate should not become turbid. On making sure that precipitation is complete, separate precipitate 1 containing the Group III sulphides and hydroxides from supernatant 1 containing cations of Groups I and II.

Precipitate 1: Group III sulphides and hydroxides (see Note 1 at the end of the Section); analyze as in *P* 5.

Supernatant 1: cations of Groups I and II and an excess of ammonium salts (see Note 2 below); analyze as described in *P* 4.

4. Preparation of supernatant 1 for tests for cations of Groups I and II. To supernatant 1 add concentrated HCl solution drop by drop until the solution is acidic to litmus. Boil the mixture to remove H_2S completely. To test for completeness of removal of H_2S, hold a piece of filter paper on which 2 or 3 drops of $Pb(CH_3COO)_2$ and 2 or 3 drops of 2*N* NaOH or KOH solution have been placed over the boiling solution; the paper should not turn black. If a precipitate is formed, centrifuge and discard the precipitate. Transfer the supernatant containing cations of Groups I and II to an evaporating dish, evaporate to dryness, and ignite until white fumes no longer evolve, i.e., until the ammonium salts are removed. Then cool the dish, crush the residue with a stirring rod and dissolve it in 3-8 ml of 2*N* CH_3COOH solution. Test the resulting solution for the presence of Group I and Group II cations as described in Sec. 36, *P* 2.

5. Dissolving of precipitate 1.[1] Transfer precipitate 1 containing the Group III sulphides and hydroxides as com-

[1] Precipitate 1 should be dissolved in a fume cupboard.

pletely as possible to an evaporating dish. 5-6 ml of NHO_3 solution (sp gr 1.2) can be used for this purpose. Add to the mixture 2 or 3 tiny crystals of KNO_2 or $NaNO_2$ (to dissolve nickel and cobalt sulphides) and heat until the black particles disappear. If they fail to disappear, add 2 or 3 crystals of KNO_2 and boil until the sulphides are completely oxidized (the black particles disappear).

6. Separation of Group III trivalent cations from the bivalent cations. To the solution obtained as described in Procedure 5 add concentrated NH_4OH solution until the solution is strongly alkaline to litmus. Stir the mixture carefully with a glass rod and boil for 1-2 minutes, stirring constantly. Centrifuge and separate precipitate 2 containing the hydroxides of Group III trivalent cations from supernatant 2 containing manganous ions and nickel, cobalt, and zinc ammines.

Precipitate 2: ferric, aluminium, and chromium hydroxides; analyze as described in *P* 11 et seq.

Supernatant 2: manganous ion and nickel, cobalt, and zinc ammines (see Note 3 at the end of the Section); analyze as described below in *P* 7 et seq.

7. Tests for nickel and cobalt ions. To 5-8 drops of supernatant 2 add 2*N* H_2SO_4 solution until the solution is acidic to litmus. Add 2 or 3 tiny crystals of NaF or KF. Divide the resulting solution into two portions. To one of them add 3-5 drops of dimethylglyoxime and 2*N* NH_4OH solution a drop at a time until the solution is alkaline. The appearance of a bright red precipitate confirms the presence of nickel ions. To the other portion of the supernatant add 2 or 3 drops of $ZnSO_4$ solution and 3 or 4 drops of $(NH_4)_2[Hg(SCN)_4]$ solution. Stir the mixture with a glass rod. The appearance of a blue precipitate indicates the presence of cobalt ions.

Cobalt ions can also be detected with the aid of another test, using NH_4SCN or KSCN (see Sec. 61, *P* 1).

8. Test for manganous ion, Mn^{2+}. If the Mn^{2+} ion was detected in the preliminary test, it is not necessary to carry out a confirmatory test for the presence of Mn^{2+} ions (see Sec. 58, *P* 1 or 2).

9. Separation of zinc ions from nickel, cobalt, and manganous ions. Heat the remainder of supernatant 2 to the boiling point and add 6*N* alkali hydroxide solution to it

until it is strongly alkaline. Boil the mixture for 2-3 minutes and centrifuge. Separate precipitate 3 containing nickel, cobalt, and manganous hydroxides from supernatant 3 containing sodium or potassium zincate. Discard the precipitate and test for the zinc ion in supernatant 3 (see *P* 10).

10. Test for zinc ion. To 5-8 drops of clear supernatant 3 add 6*N* CH_3COOH solution until the solution is acidic to litmus and pass hydrogen sulphide into it. The appearance of a white precipitate confirms the presence of zinc ions (see Note 5 at the end of the Section).

11. Separation of iron ions from aluminium and chromium ions. Wash precipitate 2 with hot water, transfer it to an evaporating dish, add 2-3 ml of 6*N* alkali hydroxide solution and 5-8 drops of 3 per cent H_2O_2 solution. Boil the mixture to complete decomposition of H_2O_2 (gas bubbles are no longer liberated), centrifuge, and separate precipitate 4 containing ferric hydroxide from supernatant 4 containing aluminate and chromate ions. Discard the precipitate and analyze the supernatant as described below in *P* 12 and *P* 13.

12. Confirmatory test for chromium ion. A yellow coloration of the supernatant indicates the presence of chromium ions. The confirmatory test is carried out as described in Sec. 56, *P* 4.

13. Tests for aluminium ion. Aluminium is detected by one of the following tests:

(a) to 2-3 ml of supernatant 4 add 2*N* H_2SO_4 solution, stirring constantly with a glass rod, until the solution is acidic to litmus, then add concentrated ammonia solution until it is weak-alkaline. Boil the mixture for 1-2 minutes. In the presence of aluminium a white flaky precipitate of aluminium hydroxide, $Al(OH)_3$, will appear;

(b) to 1-2 ml of supernatant 4 add solid NH_4Cl in small portions. Boil the mixture after the addition of each successive portion of NH_4Cl until ammonia is no longer liberated. The appearance of a white flaky precipitate indicates the presence of aluminium ions;

(c) aluminium can also be detected with the aid of the Alizarin-S reagent (see Sec. 55, *P* 2).

Note 1. The wet precipitate 1 containing the Group III sulphides is readily oxidized in the air to form soluble sul-

phates. The precipitate should therefore be separated immediately from the solution and dissolved at once (as described above in *P* 5 et seq.).

Note 2. Treat supernatant 1 immediately after separating the precipitate containing the Group III cations because $(NH_4)_2S$ is oxidized in the air to form the SO_4^{2-} ion as a result of which Group II cations, especially Ba^{2+} and Sr^{2+}, are precipitated as sulphates.

Note 3. When supernatant 2 stands for a long period of time, Mn^{2+} is oxidized to MnO(OH), and $[Co(NH_3)_6]^{2+}$ to the more stable $[Co(NH_3)_6]^{3+}$ in which the cobalt ion cannot be detected in the usual way. Therefore, immediately after separating precipitate 2 containing the hydroxides of the trivalent cations of Group III, proceed to analyze supernatant 2 (as described in *P* 7).

Note 4. Any iron ions present in the solution under test interfere with the detection of nickel and cobalt. Fe^{3+} ions should be bound in a complex with the fluoride of an alkali metal.

Note 5. If the sulphide precipitate is white in colour it is clear that it consists of ZnS and no confirmatory test is necessary. However, on making the test for zinc ion, the precipitate obtained may be black due to the presence of traces of Ni^{2+} and Co^{2+}. In this case dissolve the precipitate in 2*N* HCl solution, centrifuge the mixture, and add 2*N* NaOH solution to the resulting supernatant until it is strongly alkaline. Heat the mixture to boiling, centrifuge, discard the black precipitate consisting of CoS and NiS, acidify the supernatant with acetic acid until the solution is acidic to litmus and pass hydrogen sulphide into it again. The appearance of a white flaky precipitate confirms the presence of Zn^{2+} ion.

63. Rapid Method of Analysis of Mixture of Group III Cations

1. Preliminary tests. In separate portions of the solution under analysis carry out tests for Fe^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+} ions (see Sec. 62, *P* 2).

2. Tests for Ni^{2+} and Co^{2+} ions. To 1-2 ml of the solution under test add 6*N* NH_4OH solution until the mixture is

strongly alkaline to litmus. Centrifuge The Co^{2+}, Ni^{2+}, and Zn^{2+} ions will be present in the supernatant. Add 2*N* HCl to it until the solution is slightly acidic. Divide the solution into two portions. To one of them add 2 or 3 drops of dimethylglyoxime solution and 2*N* NH_4OH until the solution is weak-alkaline. The appearance of a bright red precipitate indicates the presence of nickel ions. To the other portion of the slightly acidic solution add 1 or 2 drops of $ZnSO_4$ solution and 3 or 4 drops of $(NH_4)_2[Hg(SCN)_4]$. Shake up the mixture and scratch the inner walls of the test tube with a glass rod. A blue precipitate will appear if cobalt ions are present. Cobalt ions can also be detected by using a saturated aqueous solution of NH_4SCN in the presence of amyl alcohol or a solution of NH_4SCN in acetone (see Sec. 61, *P* 1).

3. Separation of aluminium and zinc ions from the other cations. To 1-2 ml of the solution under test add 2*N* NaOH until the solution is strongly alkaline. Boil the mixture for 1-2 minutes and centrifuge. Al^{3+} and Zn^{2+} ions will be present in the supernatant in the form of an aluminate and a zincate. Divide the supernatant into two portions.

Test for zinc ion. Acidify one portion of the supernatant with 2*N* CH_3COOH until the solution is acidic to litmus, add the formiate buffer solution, and pass H_2S into the solution. The appearance of a white precipitate, ZnS, confirms the presence of Zn^{2+} ions.

Test for aluminium ion. To the other portion of the supernatant add solid NH_4Cl in small portions until, on boiling, NH_3 is no longer evolved (see Sec. 55, *P* 1). The appearance of a white amorphous precipitate, $Al(OH)_3$, confirms the presence of Al^{3+} ions. Aluminium can also be detected with the aid of the Alizarin-S reagent (see Sec. 55, *P* 2).

64. Analysis of Mixture of Cations of Groups I, II, and III in the Presence of Phosphate Ions

The phosphates of Groups II and III and also magnesium phosphate are not soluble in water but dissolve in strong acids. The phosphates of Group II and of the bivalent metals of Group III are soluble in acetic acid as well, whereas the phosphates of the trivalent metals of Group III ($AlPO_4$, $FePO_4$ and $CrPO_4$) do not dissolve in acetic acid. Cobalt,

nickel, and zinc phosphates are, moreover, soluble in ammonia solution.

Group III cations are precipitated by ammonium sulphide or hydrogen sulphide in an alkaline solution. In the presence of phosphate ions the phosphates of the alkaline earth metals and magnesium pass over into the precipitate together with the Group III sulphides. To avoid this it is necessary to remove the PO_4^{3-} ions. This is attained by adding a precipitant, for example, $FeCl_3$.

The analysis is carried out in the following order:

1. Test for phosphate ion. To 4 or 5 drops of the solution under test add 1 ml of 2*N* HNO_3 solution and 1 ml of ammonium molybdate, $(NH_4)_2MoO_4$. Heat the mixture to boiling and allow to stand for 2-3 minutes. The appearance of a yellow precipitate indicates the presence of phosphate ions.

2. Preliminary tests. In separate portions of the solution under analysis carry out tests (rapid method) for Fe^{3+}, Fe^{2+}, Mn^{2+}, Cr^{3+}, and NH_4^+ ions (see Sec. 62, *P* 2).

3. Removal of PO_4^{3-} ions and precipitation of phosphates of trivalent cations of Group III. To 3-5 ml of the solution under test add 1 or 2 drops of concentrated HNO_3 solution.[1]

Boil the mixture for 1-2 minutes. The oxidation of Fe^{2+} ions to Fe^{3+} ions is necessary to achieve complete precipitation of iron because Fe^{2+} ions are not precipitated by the PO_4^{3-} ion in an acetic acid solution. Add 2*N* ammonia solution drop by drop (to neutralize excess acid) until a small precipitate appears that does not disappear on shaking (or until the solution is alkaline to litmus). Add 2*N* HCl solution drop by drop, stirring constantly, until the solution becomes clear. Then add 1-2 g of ammonium acetate and 2-3 ml of 50 per cent CH_3COOH solution.

Al^{3+} and Cr^{3+} ions are precipitated in the presence of acetate ions. The PO_4^{3-} ions have been completely removed if the solution turns red on adding the acetate mixture. Otherwise it is necessary to add small portions of $FeCl_3$ until the liquid turns a reddish-brown. After a small excess of Fe^{3+} appears (appearance of a reddish-brown colour) add 10 ml of hot water to the mixture and boil it for 2-3 minutes, then

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[1] If Fe^{2+} ions were not detected in the preliminary test, HNO_3 need not be added.

as quickly as possible centrifuge and separate precipitate 1 from supernatant 1.

Precipitate 1: the phosphates of trivalent cations of Group III; analyze as described below in *P* 4 et seq.

Supernatant 1: bivalent cations of Group III and cations of Groups I and II; analyze as described in *P* 6 et seq.

4. Separation of iron ions from aluminium and chromium ions in precipitate 1. Wash precipitate 1 with hot water, transfer it to an evaporating dish, add 5-6 ml of 6*N* NaOH or KOH solution and 1 ml of 3 per cent H_2O_2 solution. Boil the mixture until the hydrogen peroxide is completely decomposed and centrifuge. Separate precipitate 2 from supernatant 2.

Precipitate 2: ferric hydroxide; need not be analyzed.

Supernatant 2: aluminate and chromate containing $[Al(OH)_4]^-$ and CrO_4^{2-} ions; analyze as described below in *P* 5.

5. Tests for aluminium and chromium ions. In the presence of chromium the solution is yellow.

In separate portions of the supernatant test for aluminium and chromium ions (see Sec. 62, *P* 12 and *P* 13).

6. Separation of bivalent cations of Group III from cations of Groups I and II in supernatant 1. To supernatant 1 add 2*N* HCl until the solution is acidic. Heat the mixture to boiling and slowly pass hydrogen sulphide into it. Add 2*N* NaOH until the solution is alkaline and pass H_2S into it again. Heat the mixture to boiling, centrifuge, and test for completeness of precipitation. On making sure that precipitation is complete, separate precipitate 3 from supernatant 3.

Precipitate 3: nickel, cobalt, manganese, and zinc sulphides; analyze as described below in *P* 7.

Supernatant 3: cations of Groups I and II, NH_4Cl and other ammonium salts; analyze as described in *P* 8.

7. Dissolving of precipitate 3. Dissolve precipitate 3 in HNO_3 (sp gr 1.2) in the presence of KNO_2 (see Sec. 62, *P* 5) and, on boiling, test for Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} ions (see Sec. 62, *P* 7 to *P* 10).

8. Preparation of supernatant 3 for testing for cations of Groups I and II. Carry out the analysis as described above (see Sec. 62, *P* 4).

65. Analysis of Mixture of Cations of Groups I, II, and III in the Presence of Organic Compounds

Organic compounds containing hydroxyl groups (sugar, glycerine, tartrates, and others) form stable complex compounds with Al^{3+}, Cr^{3+}, and Mn^{2+} and other ions. The hydroxides of these elements therefore are not precipitated in the presence of organic compounds, and the latter must be removed prior to the analysis of a mixture of cations of Groups I, II, and III.

The organic compounds are eliminated by oxidation with a mixture of sulphuric and nitric acids.

The analysis is carried out in the following order:

1. Test for organic substances. Place in a hard glass tube of small bore, closed at one end, a small amount of the substance under test (finely ground) and heat at first gently and then more strongly. In the presence of organic matter, charring takes place; the substance in the tube becomes black and a tarry deposit is produced in the upper, cold portion of the tube. If the substance to be analyzed is a liquid, it must be evaporated to dryness prior to testing for the presence of organic compounds.

2. Removal of organic compounds. Place 0.2-0.3 g of the ground substance under test in an evaporating dish and add to it 5-8 ml of 6*N* H_2SO_4 solution. Heat the mixture carefully. When all of the substance has been charred, let the dish cool and then add gradually, stirring thoroughly, 5 ml of concentrated HNO_3 (*work under a hood*). Heat the mixture gently for several minutes, then more strongly, and continue heating until copious white fumes of SO_3 are evolved. After allowing the substance to cool, add 3-5 ml of concentrated HNO_3 and evaporate until the fuming again occurs. Repeat this operation until the solution is completely decolourized. Then carefully evaporate the solution to dryness, allow the dish to cool, and add 10 ml of 2*N* H_2SO_4 solution. Boil the mixture for 2-3 minutes, centrifuge, and separate residue 1 containing Group II cations from supernatant 1.

Residue 1: the Group II sulphates; analyze as described in Sec. 38, *P* 5 et seq.

Supernatant 1: cations of Groups I and III and traces of calcium; analyze as described in Sec. 62, *P* 1 et seq.

66. Scheme for Analysis of the Group III Sulphides and Hydroxides in the Absence of Cobalt and Nickel

Precipitate: FeS, Fe_2S_3, MnS, ZnS, $Al(OH)_3$, $Cr(OH)_3$
Treat with 2*N* HCl solution to dissolve
Solution: $Fe^{2+}(Fe^{3+})$, Mn^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}
Treat with a mixture of 2*N* NaOH and 3 per cent H_2O_2. Sec. 62, *P* 11

Solution: AlO_2^-, ZnO_2^{2-}, CrO_4^{2-}
Treat with NH_4Cl. Sec. 62, *P* 13b

Precipitate: $Fe(OH)_3$ and $MnO(OH)_2$

Solution: ZnO_2^{2-}, CrO_4^{2-}
Add CH_3COOH until the solution is acidic and pass H_2S into it
White precipitate: ZnS
Sec. 62, *P* 10

Precipitate: $Al(OH)_3$ (white)

Questions and Exercises

1. How do the analytical properties of Group III cations differ from the properties of Group I and Group II cations?
2. In the form of what compounds are Group III cations precipitated by the action of $(NH_4)_2S$ in the presence of NH_4OH?
3. What Group III cations form amphoteric hydroxides?
4. What properties do amphoteric hydroxides have?
5. How are the amphoteric properties of the hydroxides of certain Group III cations utilized in the systematic analysis of this group?
6. How are Al^{3+} ions separated from Zn^{2+} ions?
7. Draw up a scheme for separating and detecting the following cations: (a) Al^{3+}, Cr^{3+}, Zn^{2+}; (b) Fe^{3+}, Mn^{2+}, Zn^{2+}; when separating the ions, the least number of operations should be carried out.
8. Write the equations for the following reactions: (a) $MnO_4^- + Fe^{2+} + H^+$; (b) $Mn^{2+} + Pb_3O_4 + H^+$; (c) $Cr_2O_7^{2-} + H_2S + H^+$; (d) $Cr^{3+} + Cl_2 + KOH$; (e) $NO_3^- + Fe^{2+} + H^+$.

CHAPTER XVI

Group IV Cations

(Ag^+, Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+})

67. Group Characteristics

The cations constituting Group IV are silver, mercury, lead, bismuth, copper, and cadmium. The Group IV sulphides are insoluble in water and in dilute acids (except ni-

tric acid) and in ammonium polysulphide. Group IV is divided into two subgroups: the silver subgroup and the copper subgroup. The chlorides of the elements included in the silver subgroup (Ag^+, Hg_2^{2+}, Pb^{2+}) are insoluble in water, whereas the chlorides of the elements of the copper subgroup (Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}) are soluble in water.

Because of the relatively high solubility of lead chloride in water, in the course of analysis of Group IV cations, Pb^{2+} ions are found in both subgroups.

68. Silver Subgroup

(Silver, Mercurous, and Lead Ions)

The Ag^+, Hg_2^{2+} and Pb^{2+} ions form with F^-, NO_3^-, NO_2^-, CH_3COO^-, ClO_3^-, ClO_4^- and MnO_4^- ions compounds that are soluble in water; and with Cl^-, Br^-, I^-, CN^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-} ions, compounds that are only sparingly soluble in water.

The cations of the silver group are separated from the cations of the copper subgroup and the cations of all the other groups by the action of hydrochloric acid on solutions of their salts.

69. Reactions of Cations of the Silver Subgroup

Tabulate the test results for the silver subgroup in the following form:

Reagents	Cations		
	Ag^+	Pb^{2+}	Hg_2^{2+}
Hydrochloric acid, HCl. [Action of ammonia solution and hot water on the precipitate formed by the action of HCl]			
Sodium hydroxide, NaOH			
Ammonia solution, NH_4OH			
Potassium iodide, KI			
Potassium chromate, K_2CrO_4			
Hydrogen sulphide, H_2S			

1. Hydrochloric acid and soluble chlorides form with the ions of the silver subgroup white precipitates: AgCl, Hg_2Cl_2.

$PbCl_2$ which do not dissolve in nitric acid. Lead chloride dissolves in hot water; silver chloride dissolves in ammonia solution to form the complex salt $[Ag(NH_3)_2]Cl$ which is soluble in water:

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$$
$$AgCl + 2NH_4OH = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

The white precipitate of univalent mercury, Hg_2Cl_2, turns black on reacting with ammonia solution due to the formation of metallic mercury:

$$Hg_2Cl_2 + 2NH_4OH = NH_2HgCl + Hg + NH_4Cl + 2H_2O$$
$$Hg_2Cl_2 + 2NH_4OH = NH_2HgCl + Hg + NH_4^+ + Cl^- + 2H_2O$$

Amino mercuric chloride, NH_2HgCl, is insoluble.

Procedure. In separate test tubes place 2 or 3 drops of solutions of a silver, a mercurous, and a lead salt. To the contents of each test tube add 2 or 3 drops of 2*N* HCl solution. A white precipitate will appear in all three test tubes: AgCl, Hg_2Cl_2, and $PbCl_2$.

Transfer a portion of the precipitates to clean test tubes; treat with ammonia solution. To the other portion of these precipitates add 5-8 drops of water and heat to boiling. The precipitate of AgCl dissolves in ammonia solution; the white precipitate of Hg_2Cl_2 on reacting with the ammonia solution turns black; $PbCl_2$ dissolves in hot water.

2. Alkali hydroxides with Ag^+ and Hg_2^{2+} ions form the oxides, Ag_2O which is brown in colour and Hg_2O which is black in colour. Their hydroxides are unstable and decompose the moment they are formed to produce the oxide and water:

$$Ag^+ + OH^- = AgOH; \quad 2AgOH = Ag_2O + H_2O$$
$$Hg_2^{2+} + 2OH^- = 2HgOH; \; 2HgOH = Hg_2O + H_2O$$

Silver oxide, Ag_2O, and mercurous oxide, Hg_2O, do not dissolve in excess alkali but dissolve in nitric acid. Silver oxide, moreover, is soluble in ammonia solution:

$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$$

An alkali hydroxide precipitates an equivalent amount of lead ions in the form of the hydroxide, $Pb(OH)_2$, which is

white and dissolves in excess alkali to form the plumbite:

$$PbCl_2 + 2NaOH = Pb(OH)_2 + 2NaCl$$
$$Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O$$

Procedure. To 2 or 3 drops of a silver, a mercurous, and a lead salt placed in separate test tubes add 2 or 3 drops of an alkali hydroxide. Note the colour of the precipitates formed. Add ammonia solution to the silver oxide; it will dissolve. Treat the lead hydroxide precipitate with an alkali hydroxide in which it will dissolve.

3. Ammonia solution added dropwise to a solution of a silver salt precipitates Ag_2O black-brown in colour; it readily dissolves in excess ammonia to form the complex ion $[Ag(NH_3)_2]^+$:

$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$$
$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]^+ + 2OH^- + 3H_2O$$

On adding ammonia solution to a mercurous salt, a black precipitate is formed, consisting of a mixture of powdery metallic mercury and white amino mercuric nitrate, NH_2HgNO_3:

$$Hg_2(NO_3)_2 + 2NH_4OH = NH_2HgNO_3\downarrow + Hg\downarrow + NH_4NO_3 + 2H_2O$$
$$Hg_2^{2+} + 2NO_3^- + 2NH_4OH = NH_2HgNO_3\downarrow + Hg\downarrow + NO_3^- + NH_4^+ + 2H_2O$$

Ammonia solution forms with Pb^{2+} ion a white precipitate of the basic salt, for example, Pb(OH)Cl, which does not dissolve in excess ammonia solution:

$$Pb(NO_3)_2 + NH_4OH = Pb(OH)NO_3 + NH_4NO_3$$
$$Pb^{2+} + NO_3^- + NH_4OH = Pb(OH)NO_3 + NH_4^+$$

Procedure. In three separate test tubes place 2 or 3 drops of a silver, a mercurous and a lead salt. Add $2N$ NH_4OH solution drop by drop. The silver oxide precipitated is dissolved in excess ammonia solution; mercurous oxide and lead hydroxide are not dissolved.

4. Potassium iodide forms the pale yellow precipitate of silver iodide, AgI, the greenish-yellow precipitate of mercurous iodide, Hg_2I_2, and the yellow crystalline precipitate of lead iodide, PbI_2. The latter, unlike AgI and Hg_2I_2, dissolves in hot water. On cooling the resulting solution, PbI_2 is reprecipitated in the form of golden-yellow crystals.

Procedure. To 2 or 3 drops of solutions of a silver, a mercurous and a lead salt, placed in separate test tubes, add 2 or 3 drops of 2*N* KI solution. Note the colour of the resulting precipitates in the laboratory notebook. Heat the test tube containing the mixture in which lead iodide was precipitated. Allow the resulting clear solution to cool slowly, as a result of which golden-yellow crystals of lead iodide will be precipitated again.

5. Potassium chromate, K_2CrO_4, forms with Ag^+, Hg_2^{2+} and Pb^{2+} ions coloured precipitates: brick-red silver chromate, Ag_2CrO_4; red mercurous chromate, Hg_2CrO_4; and yellow lead chromate, $PbCrO_4$. These precipitates dissolve readily in nitric acid. Silver chromate, moreover, is soluble in ammonia solution, and lead chromate dissolves in excess alkali.

The equation for dissolving of silver chromate in ammonia solution is

$$Ag_2CrO_4 + 4NH_4OH = [Ag(NH_3)_2]_2CrO_4 + 4H_2O$$
$$Ag_2CrO_4 + 4NH_4OH = 2[Ag(NH_3)_2]^+ + CrO_4^{2-} + 4H_2O$$

The equation for dissolving of lead chromate in an alkali hydroxide is

$$PbCrO_4 + 4NaOH = Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$
$$PbCrO_4 + 4OH^- = PbO_2^{2-} + CrO_4^{2-} + 2H_2O$$

Procedure. To 2 or 3 drops of solutions of a silver, a mercurous and a lead salt, placed in separate test tubes, add 2 or 3 drops of K_2CrO_4 solution. Coloured precipitates will appear in all three test tubes.

6. Hydrogen sulphide produces the black sulphides, Ag_2S, Hg_2S, and PbS. Mercurous sulphide decomposes to form mercuric sulphide and metallic mercury:

$$Hg_2S = HgS + Hg$$

Mercuric sulphide, HgS, is not soluble in dilute nitric acid, while the lead and silver sulphides, on heating, dissolve in 2*N* HNO_3 solution to produce the corresponding nitrate, sulphur, and nitric oxide:

$$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O$$

$$\begin{array}{r|l} 3 & PbS - 2e = Pb^{2+} + S \\ 2 & NO_3^- + 4H^+ + 3e = NO + 2H_2O \end{array}$$

$$3PbS + 8HNO_3 = 3Pb^{2+} + 6NO_3^- + 2NO + 3S + 4H_2O$$

PbS when heated with concentrated nitric acid is oxidized to the sulphate; nitric acid is reduced to nitrogen peroxide:

$$PbS + 8HNO_3 = PbSO_4 + 8NO_2 + 4H_2O$$

$$\begin{array}{c|l} 1 & PbS + 4H_2O - 8e = PbSO_4 + 8H^+ \\ 8 & NO_3^- + 2H^+ + e = NO_2 + H_2O \end{array}$$

Procedure. Place 2 or 3 drops of solutions of a silver, a mercurous and a lead salt in separate test tubes and pass hydrogen sulphide into each of them. A black precipitate will appear in all the test tubes. Treat a portion of the precipitate from each test tube with $2N$ HNO_3 solution, heating the mixtures. The silver and lead sulphides are dissolved, whereas the murcury sulphide is not dissolved.

70. Silver. Test for Silver Ion, Ag^+

Hydrochloric acid with Ag^+ ions yields a white curdy precipitate of silver chloride, AgCl, that dissolves in ammonia solution, in potassium cyanide, KCN, and in sodium thiosulphate, $Na_2S_2O_3$, to form the complex ions $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, and $[Ag(S_2O_3)_2]^{3-}$, respectively. On acidifying the resultant ammoniacal solution of silver chloride with nitric acid or on adding KI, a precipitate appears: in the first case, a white precipitate, AgCl; in the second, a pale yellow precipitate, AgI, which is much less soluble than AgCl.

The equation for the reaction of the complex silver ammine with nitric acid is

$$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl\downarrow + 2NH_4NO_3$$

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ = AgCl\downarrow + 2NH_4^+$$

The equation for the reaction of silver ammine with potassium iodide is

$$[Ag(NH_3)_2]Cl + KI + 2H_2O = AgI\downarrow + KCl + 2NH_4OH$$

$$[Ag(NH_3)_2]^+ + I^- + 2H_2O = AgI\downarrow + 2NH_4OH$$

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of $2N$ HCl solution. Decant the clear supernatant liquid and dissolve the precipitate in ammonia solution (NH_4OH should be added a drop at a time). To the resulting

clear ammoniacal solution add 2*N* HNO_3 until the solution is acidic to litmus or add KI solution; in the presence of silver the solution will become turbid.

71. Mercury. Tests for Mercurous Ion, Hg_2^{2+}

Mercury forms mercurous and mercuric compounds in which it is monovalent and bivalent, respectively. Bivalent mercury in aqueous solutions yields the Hg^{2+} ion, and monovalent mercury yields the Hg_2^{2+} or Hg^{+} ion.

1. Hydrochloric acid forms with Hg_2^{2+} a white precipitate of mercurous chloride, Hg_2Cl_2, (calomel) which turns black when treated with ammonia solution.

Procedure. To 2 or 3 drops of the solution under test placed in a test tube add 3 or 4 drops of 2*N* HCl solution and centrifuge. Treat the white precipitate of the chloride with ammonia solution. In the presence of mercurous ions the precipitate will turn black.

2. Stannous chloride[1] reduces mercurous and mercuric ions to metallic mercury in the form of a black precipitate:

$$Hg_2Cl_2 + H_2[SnCl_4] = 2Hg\downarrow + H_2[SnCl_6]$$

$$Hg_2Cl_2 + [SnCl_4]^{2-} = 2Hg\downarrow + [SnCl_6]^{2-}$$

Procedure (spot test). Place a drop of the solution under test and a drop of stannous chloride on a strip of filter paper. In the presence of mercury ions a black spot will appear.

72. Lead. Tests for Lead Ion, Pb^{2+}

Lead forms compounds in which it is bivalent and tetravalent.

1. Potassium iodide precipitates lead iodide, PbI_2, which is yellow in colour and soluble in hot water. On cooling the solution, PbI_2 is reprecipitated as flaky crystals of a golden-yellow colour.

Procedure. On adding 1 or 2 drops of KI to 2 or 3 drops of the solution under test, a yellow precipitate will appear. Heat the mixture to boiling. If the precipitate does not dis-

[1] Sn^{2+} and Sn^{4+} in hydrochloric acid solution are present in the form of complex ions, $[SnCl_4]^{2-}$ and $[SnCl_6]^{2-}$.

solve completely, centrifuge. Transfer the supernatant by means of a dropper pipette to another test tube and allow it to cool slowly. The appearance of a golden-yellow precipitate confirms the formation of PbI_2.

2. **Sulphuric acid and soluble sulphates** precipitate Pb^{2+} as lead sulphate, $PbSO_4$. The white precipitate obtained is soluble in alkali hydroxides and in ammonium acetate and tartrate solutions.

3. **Potassium chromate** precipitates lead chromate, $PbCrO_4$, as a yellow precipitate insoluble in acetic acid and in hydrochloric acid but soluble in alkali hydroxides and nitric acid.

73. Analysis of Mixture of Cations of the Silver Subgroup

The separation of cations of the silver subgroup from other cations is based on the insolubility in water of AgCl, Hg_2Cl_2, and $PbCl_2$.

Since lead is appreciably soluble in cold water, the addition of Cl^- ions at a low concentration of Pb^{2+} ions may fail to precipitate $PbCl_2$. At high concentrations of Pb^{2+} ions, $PbCl_2$ is precipitated, although not completely.

Hydrochloric acid for precipitation of chlorides should be added in the form of a dilute solution and in a small excess in order to achieve completeness of precipitation of the chlorides and to keep the precipitate from passing into the colloidal state. A large excess of HCl, in particular concentrated HCl, should not be added because it may cause the formation of water-soluble complex salts containing $[AgCl_3]^{2-}$ and $[PbCl_4]^{2-}$ ions, and consequently, the chlorides will not be precipitated quantitatively.

The isolation of the chlorides of the silver subgroup is based on the solubility of $PbCl_2$ in hot water and the solubility of AgCl in ammonia solution.

On treating a precipitate containing silver and mercury chlorides with an ammonia solution, silver chloride is dissolved and mercurous ions are detected because the precipitate of Hg_2Cl_2 turns black.

The analysis of cations of the silver subgroup is carried out in the following way.

1. Separation of cations of the silver subgroup from other cations. Heat 3-5 ml of the solution under test to boiling and add 1-2 ml of 2*N* HCl solution, a drop at a time, stirring vigorously. Heat the mixture to boiling once more (but do not boil), allow to cool, centrifuge, and test for completeness of precipitation. For this purpose, without separating the precipitate from the solution, carefully add a drop of 2*N* HCl solution down the wall of the test tube; this should not result in the appearance of turbidity. On attaining complete precipitation, recentrifuge the mixture (if the liquid over the precipitate is not clear) and separate precipitate 1 from supernatant 1.

Precipitate 1: silver, mercurous and lead chlorides.

Supernatant 1: solution of salts of cations of other groups.

2. Separation of lead chloride from mercurous and silver chlorides. Wash precipitate 1 one or two times with cold water. Transfer the washed precipitate to an evaporating dish or beaker and add 2-3 ml of hot water. Mix thoroughly, boil the mixture for 2-3 minutes, and immediately centrifuge. Separate residue 2 from supernatant 2.

Residue 2: silver and mercurous chlorides; analyze as described below in *P* 4.

Supernatant 2: lead chloride; analyze as follows.

3. Tests for Pb^{2+} ion in supernatant 2. The Pb^{2+} ion is detected by means of one of the following tests: (a) with KI solution (see Sec. 72, *P* 1); (b) with K_2CrO_4 solution (see Sec. 72, *P* 3).

4. Test for mercurous ions in residue 2 and dissolving of silver chloride. Wash residue 2 two or three times with hot water and add 3-5 drops of concentrated ammonia solution. Stir the mixture thoroughly with a glass rod and heat gently. If the residue turns black this indicates the presence of mercurous ions. Centrifuge.

Residue 3: metallic mercury and amino mercuric chloride; is not analyzed.

Supernatant 3: silver ammine; analyze as described below in *P* 5.

5. Test for Ag^+ ion in supernatant 3. To supernatant 3 add, with stirring, 2*N* HNO_3 until the solution is acidic to litmus. The appearance of a white precipitate or turbidity confirms the presence of silver.

74. Scheme for Analysis of the Chlorides of the Silver Subgroup

Precipitate: $PbCl_2$, Hg_2Cl_2, and AgCl
Treat with hot water and centrifuge. Sec. 73, *P* 2

Supernatant: $PbCl_2$	*Residue*: Hg_2Cl_2 and AgCl	
1. Add KI; yellow PbI_2 is precipitated; dissolve in hot water. On cooling, PbI_2 is reprecipitated as bright yellow needle-like crystals Sec. 72, *P* 1 2. Add H_2SO_4; a white precipitate is formed. Sec. 72, *P* 2	Treat with NH_4OH and centrifuge. Sec. 73, *P* 4	
	Precipitate:	*Solution*:
	$Hg\begin{matrix}NH_2\\Cl\end{matrix} + Hg$ (black)	$[Ag(NH_3)_2]Cl$ Treat with HNO_3 until the solution is acidic. Sec. 73, *P* 5. A white precipitate or turbidity, AgCl, will appear

Questions and Exercises

1. How do the analytical properties of the cations of the silver subgroup differ from those of the cations of the other groups?
2. Why can the Pb^{2+} ion be found in both subgroups of the fourth group?
3. Write the equations for the reactions of NH_4OH and NaOH with the cations of the silver subgroup.
4. Write the equation for the dissolving of $PbSO_4$ in an alkali hydroxide.
5. Describe the procedure for analyzing cations of the silver subgroup by means of equations for the chemical reactions that take place.

75. Copper Subgroup

(Copper, Mercuric, Lead, Bismuth and Cadmium Ions)

Hydrogen sulphide in an acidic solution is the group reagent for cations of the copper subgroup. The cations of this group are precipitated with hydrogen sulphide in hydrochloric acid solution (approximately 0.3*N* HCl). The sul-

phides formed by the cations of the copper subgroup (besides mercuric sulphide) are soluble in hot $2N$ HNO_3 solution.

Nitric acid, on dissolving the sulphides, acts as an oxidizing agent, and depending on the concentration of the acid, it is reduced to NO or NO_2, oxidizing the sulphide ion to free sulphur or the sulphate ion.

The equation for the reaction of dissolving of copper sulphide in $2N$ HNO_3 solution is

$$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

$$3 \mid \quad CuS - 2e = Cu^{2+} + S$$

$$2 \mid \quad NO_3^- + 4H^+ + 3e = NO + 2H_2O$$

In this reaction HNO_3 acts as an oxidizing agent and as the electrolyte yielding the NO_3^- ion which is necessary for forming soluble salts. Two moles of HNO_3 are needed to oxidize 3 moles of CuS, and 6 moles of HNO_3 are needed to dissolve 3 moles of CuS. Hence, a total amount of 8 moles of HNO_3 are needed.

S^{2-} is oxidized to SO_4^{2-} on dissolving lead sulphide in concentrated nitric acid which is reduced to nitrogen peroxide:

$$PbS + 8HNO_3 = PbSO_4 + 8NO_2 + 4H_2O$$

$$1 \mid \quad PbS + 4H_2O - 8e = PbSO_4 + 8H^+$$

$$8 \mid \quad HNO_3 + H^+ + e = NO_2 + H_2O$$

Alkali hydroxides precipitate the cations of the copper subgroup (besides Hg^{2+}) as hydroxides which are readily dehydrated and converted to the respective oxides that are insoluble in alkali hydroxides[1].

Ammonia reacts with all the cations of the copper subgroup (except mercuric ions) to form basic salts. The basic salts of copper and cadmium dissolve in excess ammonia to form complex ammines, $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_6]^{2+}$. Hg^{2+} ions react with ammonia to form the insoluble amino salt NH_2HgCl.

Most of the salts of the cations of the copper subgroup, with the exception of nitrates, nitrites, chlorides[2], acetates, and sulphates[3] are insoluble in water.

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[1] Lead hydroxide is soluble in alkalies.
[2] Lead chloride is slightly soluble in cold water,
[3] Lead sulphate is insoluble in water.

76. Reactions of Cations of the Copper Subgroup

Tabulate the test results for cations of the copper subgroup in the following form:

Reagents	Cations				
	Hg^{2+}	Pb^{2+}	Bi^{3+}	Cu^{2+}	Cd^{2+}
Hydrogen sulphide, H_2S, (treat the sulphides obtained with $2N$ HNO_3 solution with heating)					
Sodium hydroxide, NaOH, taken:					
in an equivalent quantity					
in excess					
Ammonia solution, NH_4OH, taken:					
in an equivalent quantity					
in excess					
Potassium iodide, KI					

1. Hydrogen sulphide converts all the cations of the copper subgroup to insoluble sulphides. PbS and CuS are black precipitates. Bi_2S_3 is a dark brown precipitate. The colour of CdS depends on the acidity of the solution; a pale yellow precipitate is formed in neutral or slightly acidic solutions, while precipitates that vary in colour from orange-yellow to brown are obtained from strongly acidic solutions ($pH < 0.4$) with heating. When H_2S acts on Hg^{2+} salts, a white precipitate is formed at first. As hydrogen sulphide is further passed into the mixture, the precipitate turns yellow, then brown and finally black. The precipitate changes colour due to the formation of intermediate products, such as $HgCl_2 \cdot 2HgS$. The final product is black mercuric sulphide, HgS. The white precipitate appears as a result of the reaction

$$3HgCl_2 + 2H_2S = HgCl_2 \cdot 2HgS\downarrow + 4HCl$$

$$3HgCl_2 + 2H_2S = HgCl_2 \cdot 2HgS\downarrow + 4H^+ + 4Cl^-$$

When additional hydrogen sulphide is passed into the mixture, the following reaction occurs:

$$HgCl_2 \cdot 2HgS + H_2S = 3HgS + 2H^+ + 2Cl^-$$

The sulphides of lead, copper, cadmium, and bismuth dissolve in $2N$ HNO_3 solution.

Cadmium sulphide, unlike the sulphides of copper and bismuth, dissolves (when heated) in 2*N* HCl solution. Copper and bismuth sulphides dissolve only in concentrated HCl.

The equation for the reaction of dissolving of bismuth sulphide in nitric acid is

$$Bi_2S_3 + 8HNO_3 = 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$$

$$\begin{array}{rl} 1 & Bi_2S_3 - 6e = 2Bi^{3+} + 3S \\ 2 & NO_3^- + 4H^+ + 3e = NO + 2H_2O \end{array}$$

$$Bi_2S_3 + 2NO_3^- + 8H^+ = 2Bi^{3+} + 3S + 2NO + 4H_2O$$

The dissolving of copper and cadmium sulphides proceeds similarly.

Mercuric sulphide differs from the other sulphides of the copper subgroup in that it does not dissolve on heating it in 2*N* HNO_3 solution, but it dissolves in strong oxidizing agents such as concentrated nitric acid, aqua regia, and in dilute hydrochloric acid in the presence of an oxidizing agent, for instance, hydrogen peroxide. Mercuric sulphide also dissolves in a solution of K_2S or Na_2S, and does not dissolve in an ammonium sulphide or ammonium polysulphide solution.

The reaction of dissolving of mercuric sulphide in aqua regia is

$$3HgS + 6HCl + 2HNO_3 = 3HgCl_2 + 3S + 2NO + 4H_2O$$

In this reaction the hydrochloric acid in aqua regia (consisting of 3 volumes of HCl and 1 volume of HNO_3), on being heated, is oxidized by the nitric acid to free chlorine which at the moment of its liberation oxidizes HgS to $HgCl_2$ and free sulphur:

$$3HCl + HNO_3 = 3Cl^0 + NO + 2H_2O$$

$$\begin{array}{rl} 3 & HCl - e = Cl^0 + H^+ \\ 1 & NO_3^- + 4H^+ + 3e = NO + 2H_2O \end{array}$$

$$3Cl^- + NO_3^- + 4H^+ = 3Cl^0 + NO + 2H_2O$$

$$3HgS + 6Cl^0 = 3HgCl_2 + 3S$$

On dissolving mercuric sulphide in a solution of a sulphide of an alkali metal, a complex salt is formed:

$$HgS + K_2S = K_2[HgS_2]$$

Procedure. Pass a slow stream of hydrogen sulphide into separate test tubes containing solutions of mercuric, lead, copper, cadmium, and bismuth salts; a precipitate will appear in all the test tubes. The precipitate in the test tube with a solution of a mercuric salt will first be white, then turn yellow, brown, and finally, black. The precipitates in the test tubes with solutions of lead and copper salts are black; bismuth salts form dark brown precipitates; cadmium salts, yellow precipitates. Divide each of the precipitates obtained into several portions in separate test tubes, add to different precipitates a few drops of 2*N* HNO_3 and heat. All the precipitates, with the exception of HgS, are dissolved in the acid. Treat the cadmium sulphide precipitate with 2*N* HCl solution; it will dissolve on heating. In another test tube boil the mercuric sulphide precipitate for 1-2 minutes with 2*N* HCl solution and a few drops of hydrogen peroxide; the precipitate will be dissolved.

2. An alkali added in a small quantity to the solution of a mercuric salt forms a red-brown basic salt, for example, basic mercuric nitrate, $Hg(OH)NO_3$, (subnitrate). On adding more alkali, mercuric hydroxide, $Hg(OH)_2$, is formed which decomposes to form yellow mercuric oxide and water:

$$Hg(NO_3)_2 + NaOH = Hg(OH)NO_3 + NaNO_3$$
$$Hg^{2+} + OH^- = [Hg(OH)]^+$$
$$Hg(OH)NO_3 + NaOH = Hg(OH)_2 + NaNO_3$$
$$Hg(OH)^+ + OH^- = Hg(OH)_2$$
$$Hg(OH)_2 = HgO + H_2O$$

Copper, cadmium, and bismuth are precipitated by alkalies from the solutions of their salts in the form of flocculent precipitates of the hydroxides of the following colours: blue $Cu(OH)_2$, white $Cd(OH)_2$ and $Bi(OH)_3$. None of these precipitates dissolve in excess alkali.

Procedure. Place 2 or 3 drops of solutions of a copper, a cadmium, and a bismuth salt into separate test tubes. Add to each test tube 2 or 3 drops of 2*N* alkali hydroxide. A precipitate will appear in all the test tubes: yellow HgO, blue $Cu(OH)_2$, white $Cd(OH)_2$ and $Bi(OH)_3$.

3. Ammonia solution forms with solutions of mercuric salts amino mercuric chloride, NH_2HgNO_3; this white pre-

cipitate is insoluble in excess ammonium hydroxide:

$$Hg(NO_3)_2 + 2NH_4OH = NH_2HgNO_3 + 2H_2O + NH_4^+ + NO_3^-$$

Ammonia solution in a small quantity forms with Cu^{2+} ions a greenish-blue precipitate of a basic salt that is readily soluble in excess ammonium hydroxide. On dissolving, the solution turns a deep blue colour due to the presence of $[Cu(NH_3)_4]^{2+}$ ion. This is a test for the Cu^{2+} ion. The equations for the reaction are:

$$2CuSO_4 + 2NH_4OH = Cu_2(OH)_2SO_4 + (NH_4)_2SO_4$$

$$2Cu^{2+} + 2SO_4^{2-} + 2NH_4OH = Cu_2(OH)_2SO_4 + 2NH_4^+ + SO_4^{2-}$$

$$Cu_2(OH)_2SO_4 + (NH_4)_2SO_4 + 6NH_4OH = 2[Cu(NH_3)_4]SO_4 + 8H_2O$$

$$Cu_2(OH)_2SO_4 + 2NH_4^+ + 6NH_4OH = 2[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 8H_2O$$

Ammonia solution added to a solution of a cadmium salt in an equivalent quantity forms with cadmium ion cadmium hydroxide, $Cd(OH)_2$, a white precipitate that readily dissolves in excess ammonium hydroxide to form the colourless complex ion $[Cd(NH_3)_4]^{2+}$:

$$Cd(OH)_2 + 4NH_4OH = [Cd(NH_3)_4]^{2+} + 2OH^- + 4H_2O$$

Bismuth ions are precipitated by ammonia solution in the form of a white precipitate of a basic bismuth salt, for example, $Bi(OH)SO_4$.

Procedure. To 2 or 3 drops of solutions of mercuric, copper, cadmium, and bismuth salts placed in separate test tubes add *2N* ammonia solution drop by drop. Hg^{2+} and Bi^{3+} ions produce white precipitates that do not dissolve in excess ammonium hydroxide. Copper and cadmium salts with small quantities of ammonia solution form precipitates: Cu^{2+} ions, a greenish-blue precipitate; Cd^{2+} ions, a white precipitate. Both precipitates are readily dissolved in excess ammonia solution; the copper ions colour the solution a dark blue, while the cadmium ions give a colourless solution.

4. Potassium iodide (in a small quantity) forms with a solution of a mercuric salt a red precipitate of mercuric iodide, HgI_2, which dissolves in excess KI to form the complex salt $K_2[HgI_4]$:

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

$$HgI_2 + 2KI = K_2[HgI_4]$$

$K_2[HgI_4]$ is a colourless salt. It is dissociated according to the equation

$$K_2[HgI_4] \rightleftarrows 2K^+ + [HgI_4]^{2-}$$

A solution of $K_2[HgI_4]$ in concentrated alkali hydroxide solution (NaOH or KOH) is known as Nessler's reagent and is used as a sensitive reagent for confirming the presence of ammonium ions and ammonia (see Sec. 26, *P* 2).

Potassium iodide forms with Cu^{2+} salts a white precipitate of cuprous iodide, CuI; with Cd^{2+} salts it forms soluble complex salts of various composition, for example, $K_2[CdI_4]$; and with bismuth salts it forms a black precipitate of bismuth iodide, BiI_3.

The reaction between Cu^{2+} and I^- ions is an oxidation-reduction reaction since Cu^{2+} ions are reduced to Cu^+ ions, whereas the iodide, ions are oxidized to free iodine:

$$2Cu^{2+} + 4I^- = 2CuI\downarrow + I_2$$

The colour of cuprous iodide is masked by that of the iodine liberated and, consequently, the precipitate appears to be of a reddish-brown colour.

Procedure. To 2 or 3 drops of solutions of Hg^{2+}, Cu^{2+}, Cd^{2+}, and Bi^{3+} salts placed in separate test tubes add KI drop by drop.

Note the colour of the precipitates obtained.

77. Mercury. Test for Mercuric Ion, Hg^{2+}

The Hg^{2+} ion is colourless.

Stannous chloride, $SnCl_2$, reduces Hg^{2+} to Hg_2Cl_2 (calomel), a white, water-insoluble precipitate. On adding more $SnCl_2$, calomel is reduced to metallic mercury in the form of a black powder (see Sec. 71, *P* 2). This is a very sensitive reaction.

Procedure. To 2 or 3 drops of the solution under test add $SnCl_2$ a drop at a time. In the presence of Hg^{2+} ions, at first a white precipitate will appear; then on adding more $SnCl_2$, the precipitate will become darker and darker until it is black.

78. Copper. Tests for Cupric Ion, Cu^{2+}

Copper forms cuprous and cupric compounds in which it is respectively univalent and bivalent.

1. Ammonia solution added in excess to solutions of Cu^{2+} salts forms ammines of a dark blue colour (see Sec. 76, *P* 3).

Procedure. To 2 or 3 drops of the solution under test add 1 or 2 drops of 2*N* ammonia solution. Continue to add the ammonia solution dropwise to the suspension of the basic salt produced. In the presence of Cu^{2+} ions an intense dark blue colour will appear.

2. Potassium ferrocyanide, $K_4[Fe(CN)_6]$, forms with Cu^{2+} salts in neutral and acetic acid solutions a reddish-brown precipitate of cupric ferrocyanide, $Cu_2[Fe(CN)_6]$:

$$2CuSO_4 + K_4[Fe(CN)_6] = Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$$
$$2Cu^{2+} + [Fe(CN)_6]^{4-} = Cu_2[Fe(CN)_6]\downarrow$$

This salt is insoluble in dilute acids and is decomposed by alkalies to form $Cu(OH)_2$, a blue precipitate. $Cu_2[Fe(CN)_6]$ dissolves in ammonia solutions to form cupric ammine:

$$Cu_2[Fe(CN)_6] + 4KOH = 2Cu(OH)_2\downarrow + K_4[Fe(CN)_6]$$
$$Cu_2[Fe(CN)_6] + 4OH^- = 2Cu(OH)_2\downarrow + [Fe(CN)_6]^{4-}$$
$$Cu_2[Fe(CN)_6] + 8NH_3 = 2[Cu(NH_3)_4]^{2+} + [Fe(CN)_6]^{4}$$

Fe^{3+} ions interfere with this test because with $K_4[Fe(CN)_6]$ they form Prussian blue.

Procedure. To 2 or 3 drops of the solution under test add 3 or 4 drops of $K_4[Fe(CN)_6]$ solution. In the presence of Cu^{2+} ions a red-brown precipitate will appear.

79. Cadmium. Test for Cadmium Ion, Cd^{2+}

Cadmium is always bivalent in its compounds. The Cd^{2+} salts are colourless.

Hydrogen sulphide precipitates Cd^{2+} in neutral or slightly acidic solutions as CdS, a yellow precipitate (see Sec. 76, *P* 1).

Procedure. Pass hydrogen sulphide into a neutral or slightly acidic solution of a cadmium salt. In the presence of cadmium a yellow precipitate will appear.

80. Bismuth. Test for Bismuth Ion, Bi^{3+}

Bismuth forms compounds in which it is trivalent or pentavalent.

Stannites of alkali metals, Na_2SnO_2 and K_2SnO_2, in an alkaline solution reduce bismuth hydroxide, $Bi(OH)_3$, or bismuthyl hydroxide, BiOOH, to metallic bismuth:

$$2Bi(OH)_3 + 3Na_2SnO_2 = 2Bi + 3Na_2SnO_3 + 3H_2O$$

$$2 \mid \quad Bi(OH)_3 + 3e = Bi + 3OH^-$$

$$3 \mid \quad SnO_2^{2-} + 2OH^- - 2e = SnO_3^{2-} + H_2O$$

$$2Bi(OH)_3 + 2SnO_2^{2-} = 2Bi + 3SnO_3^{2-} + 3H_2O$$

Procedure. Prepare a fresh solution of the stannite as follows: to 1 or 2 drops of 5 per cent $SnCl_2$ solution add $2N$ NaOH or KOH solution a drop at a time until the precipitate of $Sn(OH)_2$ is almost completely dissolved. The solution should be strongly alkaline to litmus (a slight turbidity is permissible.) Then obtain a precipitate of bismuth hydroxide or the basic bismuth salt by adding an excess of alkali or ammonia solution to the solution under test. Mix the resultant white precipitate with the freshly prepared stannite solution. In the presence of bismuth the precipitate will become black.

81. Analysis of Mixture of Cations of Groups I, II, III, and IV in the Absence of Sulphates of the Alkaline Earth Metals

To separate the Group IV sulphides from the Group III sulphides it is necessary that the concentration of S^{2-} in the solution be adequate for precipitating sulphides of Groups IV and V but inadequate for precipitating Group III sulphides. Such a concentration of S^{2-} ions can be obtained by maintaining a definite concentration of hydrogen ions. On precipitating with hydrogen sulphide in a $0.3N$ HCl solution, Group IV cations can be completely separated from the cations of Groups I, II, and III. If the concentration of HCl is greater than $0.3N$, the sulphides of some of the cations of Group IV will not be precipitated at all or will be precipitated incompletely. This refers especially to CdS and PbS. If the concentration of HCl is less than $0.3N$, Group III

sulphides (for example, CoS and NiS) will be partly precipitated together with the Group IV sulphides.

The concentration of hydrochloric acid in the supernatant obtained after separating the cations of the silver subgroup is usually unknown; it is recommended, therefore, that excess hydrochloric acid be first neutralized with ammonia solution and then such a quantity of HCl be added to the resulting neutral solution as is needed to obtain a concentration of approximately $0.3N$ (pH $\approx$ 0.5).

Separation of the cations of the copper subgroup is based on their following properties: (a) the solubility of all the sulphides, with the exception of HgS, in hot dilute nitric acid; (b) the insolubility of $PbSO_4$ in water and dilute H_2SO_4; (c) the solubility of the basic salts of copper and cadmium in excess ammonia solution, whereas $Bi(OH)_3$ is insoluble in excess ammonia solution; (d) the solubility of CdS and insolubility of CuS in hot $2N$ HCl solution.

The analysis is carried out in the following order:

1. Preliminary tests. Test for presence of NH_4^+, Fe^{2+}, and Fe^{3+} ions in separate portions of the solution under test by the method of separation or isolation (see Sec. 62, *P* 2).

2. Separation of cations of the silver subgroup. To 3-5 ml of the solution under test add $2N$ HCl solution drop by drop until no additional precipitate is formed. Heat the mixture to boiling, allow to cool, centrifuge, and test for completeness of precipitation (see Sec. 73, *P* 1). On making sure that precipitation is complete, separate precipitate 1 from supernatant 1.

Precipitate 1: chlorides of cations of the silver subgroup; analyze as described below in *P* 3.

Supernatant 1: cations of Groups I, II, III, and those of the copper subgroup; analyze as described in *P* 4.

3. Analysis of the precipitate of chlorides of the silver subgroup. Wash precipitate 1 with $2N$ HCl solution. Add the wash water to supernatant 1. Analyze the precipitate as described in the analysis of cations of the silver subgroup (see Sec. 73).

4. Separation of cations of the copper subgroup from the cations of Groups I, II, and III. To supernatant 1 add concentrated ammonia solution a drop at a time (see Note 1

at the end of the Section) until the solution is slightly acidic (pH $\approx$ 3-5). If excess ammonia solution was used for neutralizing the solution (litmus paper turns blue), add 2*N* HCl solution until the solution is slightly acidic (pH $\approx$ 3-5). To the slightly acidic solution add 2-3 ml of 2*N* HCl solution (pH $\approx$ 0.5). Heat the solution to the boiling point and pass H_2S into it during 1-2 minutes. Then add an equal volume of cold distilled water or hydrogen-sulphide water and again pass H_2S into the mixture during 1-2 minutes (see Note 2 at the end of the Section). Centrifuge the mixture and test for completeness of precipitation by passing H_2S into the solution or by adding a few drops of hydrogen-sulphide water to it. If precipitation is complete, no turbidity will appear in the supernatant. After making sure that precipitation is complete, separate precipitate 2 from supernatant 2.

Precipitate 2: sulphides of the cations of the copper subgroup (see Note 3 at the end of the Section); analyze as described below in *P* 6.

Supernatant 2: cations of Groups I, II, and III and excess H_2S; analyze as described in *P* 5.

5. Preparation of supernatant 2 prior to testing for cations of Groups I, II, and III. Boil supernatant 2 to complete removal of hydrogen sulphide (filter paper moistened with lead acetate solution will not turn black when introduced into the vapours of the boiling liquid (see Sec. 62, *P* 4). Hydrogen sulphide should be removed immediately after separating supernatant 2, otherwise, on standing, S^{2-} in the solution may be oxidized by the oxygen in the air to SO_4^{2-} and a precipitate containing the insoluble Group II sulphates will be formed. After removing hydrogen sulphide, centrifuge or filter to remove sulphur. Then analyze the solution as described in Sec. 64.

6. Separation of Hg^{2+} from other cations of the copper subgroup. Wash precipitate 2 two or three times with hot water saturated with hydrogen sulphide and containing 5 per cent NH_4NO_3 (see Note 4 at the end of the Section). Transfer the washed precipitate to an evaporating dish, add to it 5-8 ml of 2*N* HNO_3 solution, and boil for 1-2 minutes. Centrifuge the mixture and separate residue 3 from supernatant 3.

Residue 3: mercuric sulphide; analyze as described below in *P* 7.

Supernatant 3: lead, bismuth, copper, and cadmium nitrates; analyze as described in *P* 8.

7. Test for Hg^{2+} cation. Wash residue 3 with hot water, transfer to an evaporating dish, add 2-3 ml of 2*N* HCl solution and 1 ml of 3 per cent hydrogen peroxide solution. Evaporate the liquid in a fume chamber until the black particles disappear and the hydrogen peroxide is decomposed (gas bubbles are no longer evolved). Avoid strong evaporation because mercuric salts are volatile. Add 3-5 drops of water and 2 or 3 drops of clear filtered $SnCl_2$ solution. The appearance of a white, grey, or black precipitate indicates the presence of mercuric ions.

8. Isolation of lead cations. Transfer supernatant 3 to an evaporating dish, add to it 2-3 ml of 2*N* H_2SO_4 solution and evaporate under a hood until copious white fumes appear (almost to dryness); excess nitric acid is removed and $PbSO_4$ is precipitated. Allow the contents of the dish to cool and add 1-2 ml of 2*N* H_2SO_4 solution. Agitate thoroughly and centrifuge. Separate precipitate 4 from supernatant 4.

Precipitate 4: lead sulphate; analyze as described below in *P* 9.

Supernatant 4: bismuth, copper, and cadmium sulphates; analyze as described in *P* 10.

9. Test for lead ions. Wash precipitate 4 with hot water 2 or 3 times, transfer to an evaporating dish, add 2-3 ml of 6*N* NaOH or KOH solution, heat to the boiling point and centrifuge. Add to the supernatant 2*N* H_2SO_4 until the solution is acidic. The appearance of a white precipitate indicates the presence of lead ions.

10. Separation of bismuth ions from copper and cadmium ions. To supernatant 4 carefully add concentrated ammonia solution drop by drop, stirring after the addition of each successive drop, until the solution is strongly alkaline to litmus. Heat to the boiling point, centrifuge, and separate precipitate 5 from supernatant 5.

Precipitate 5: the basic bismuth salt; analyze as described below in *P* 11.

Supernatant 5: copper and cadmium ammines; analyze as described in *P* 12.

11. Test for bismuth ions. Wash precipitate 5 with hot water and treat it with freshly prepared potassium or sodium stannite solution (see Sec. 80). The presence of bismuth ions is indicated if the precipitate turns black.

12. Tests for copper and cadmium ions. A blue coloration of supernatant 5 indicates the presence of copper ions. If the solution is colourless, a confirmatory test for copper ions should be made. To 3-5 drops of supernatant 5 add 2*N* CH_3COOH until the solution is acidic to litmus and 2 or 3 drops of $K_4[Fe(CN)_6]$. The appearance of a red-brown precipitate or red-brown coloration of the solution indicates the presence of copper ions. To detect cadmium ions in the absence of copper ions, pass hydrogen sulphide into supernatant 5. The appearance of a yellow precipitate indicates the presence of cadmium ions. To detect cadmium ions in the presence of copper ions, acidify supernatant 5 with concentrated HCl solution until it is acidic to litmus and pass H_2S into it. Stir the mixture thoroughly with a glass rod and heat it to the boiling point. Centrifuge. Make sure that precipitation is complete and separate the precipitate from the solution; discard the precipitate, add ammonia solution to the supernatant until it is just alkaline and pass H_2S into it.

The appearance of a yellow precipitate indicates the presence of cadmium ions (see Note 5 below).

Note 1. Concentrated ammonia solution is used for neutralizing the acid to avoid considerable dilution of the solution; when the acidity of the solution decreases or the solution becomes alkaline, a precipitate may form that either dissolves on subsequent addition of acid or is converted to the sulphide on passing H_2S into the solution.

Note 2. Hydrogen sulphide is passed into the cold diluted solution in order to completely precipitate the relatively more soluble sulphides (for example, CdS) which are not formed in hot solutions. The colour of the precipitated sulphides often indicates the presence of particular cations. A black precipitate indicates the presence of CuS, Bi_2S_3, PbS; a white or yellowish-white precipitate that turns black on continuing to pass H_2S into the solution indicates the presence of HgS; a yellow precipitate indicates the presence of CdS.

Note 3. If the sulphides are allowed to stand in the air, they are converted to water-soluble sulphates (except $PbSO_4$). Therefore, precipitate 2 containing sulphides of Group IV should be treated as described in *P* 6 just as soon as possible.

It is recommended that precipitation of the cations of Groups IV and III be started only if there is plenty of time to carry out the analysis before the precipitates pass into solution. If, however, it is necessary to interrupt work shortly after precipitation, fill the test tube containing the precipitate to the brim with hydrogen-sulphide water and close it loosely with a stopper.

Note 4. The solution for washing the precipitate is prepared as follows: dissolve 1 g of NH_4NO_3 in 200 ml of water and saturate with H_2S.

Note 5. A black precipitate may be formed, consisting of traces of mercury, bismuth, and lead sulphides. Wash the precipitate two or three times with hot water and treat with 1-2 ml of 2*N* HCl solution. Heat the mixture to boiling and centrifuge. Dilute the supernatant with 3-5 ml of water and pass H_2S into it. The appearance of a yellow precipitate indicates the presence of cadmium ions.

82. Scheme for Analysis of the Sulphides of the Copper Subgroup (see p. 180)

Questions and Exercises

1. How do the analytical properties of the cations of the silver subgroup differ from those of the cations of the copper subgroup?
2. How do the analytical properties of Group III cations differ from those of Group IV cations?
3. On passing H_2S into a solution containing the copper subgroup, what compounds are precipitated and what are their colours?
4. Why is the Hg_2^{2+} ion included in the silver subgroup, whereas the Hg^{2+} ion is included in the copper subgroup?
5. Write the equations for the reactions that occur on dissolving (a) PbS in HNO_3; (b) $PbSO_4$ in NaOH.
6. What test is used for detecting bismuth ions? Write the equation for the reaction that occurs.
7. What conclusion can be drawn if, on separating Bi^{3+} ions from Cu^{2+} and Cd^{2+} ions, no precipitate appears and the solution remains clear?

Scheme for Analysis of the Sulphides of the Copper Subgroup

Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS. Sec. 81, *P* 4
Treat with $2N$ HNO_3, boil. Sec. 81, *P* 6

Precipitate: HgS + S		*Solution*: Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}	
Treat with HCl + H_2O_2 and boil. Sec. 81, *P* 7		Add H_2SO_4 (1 : 1). evaporate until copious white fumes appear. Sec. 81, *P* 8. Allow to cool, then carefully dilute with water. Centrifuge	
Solution: Hg^{2+}	*Precipitate*: S Discard	*Solution*: Bi^{3+}, Cu^{2+}, Cd^{2+}	*Precipitate*: $PbSO_4$
Treat with $SnCl_2$. A white, grey, or black precipitate is formed. Sec. 81, *P* 7. Confirms Hg^{2+}		Add NH_4OH (excess). Sec. 81, *P* 10	Treat with NaOH or KOH with boiling. Sec. 81, *P* 9
		Precipitate: $Bi(OH)SO_4$. Sec. 81, *P* 11	*Solution*: $[Cu(NH_3)_4]^{2+}$ $[Cd(NH_3)_4]^{2+}$	*Solution*: Na_2PbO_4 + + Na_2SO_4
		Treat with alkaline solution of Na_2SnO_2 + + NaOH to precipitate black Bi. Sec. 80. Confirms Bi^{3+}	The blue colour of the solution indicates Cu^{2+}. Acidify with HCl and add H_2S to precipitate yellow CdS. Confirms Cd^{2+}	Acidify with H_2SO_4 to precipitate white $PbSO_4$. Sec. 81, *P* 9 Confirms Pb^{2+}

CHAPTER XVII

Group V Elements

(As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+})[1]

83. Group Characteristics

The elements constituting Group V are arsenic, antimony, and tin. The Group V sulphides, the same as the Group IV sulphides, are insoluble in water and in dilute acids. However, unlike most of the Group IV sulphides, they readily dissolve in solutions of the sulphides and polysulphides of alkali metals and ammonium with the formation of thiosalts. Thiosalts (they are also called sulphosalts) can be considered to be salts of the corresponding oxyacids in which oxygen is replaced by sulphur.

Each thiosalt corresponds to a particular thioacid which like carbonic acid is unstable and does not exist in the free state but decomposes to form hydrogen sulphide and the respective sulphide. Thus, the thiosalt Na_3AsS_3 corresponds to the thioacid H_3AsS_3 which is decomposed the moment it is formed according to the equation

$$2H_3AsS_3 = 3H_2S + As_2S_3$$

The solutions of thiosalts are yellow, brown, or red in colour and only a few of them are colourless. The thiosalts of alkali metals and ammonium are soluble in water. They are formed on dissolving the Group V sulphides in sulphides of alkali metals (K_2S or Na_2S) and also in ammonium sulphide, $(NH_4)_2S$, or ammonium polysulphide, $(NH_4)_2S_2$:

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

Thioacids are formed when mineral acids act on the thiosalts:

$$(NH_4)_3AsS_3 + 3HCl = H_3AsS_3 + 3NH_4Cl$$

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[1] Group V includes the elements As, Sn, Sb which have acid properties and usually occur in aqueous solution as anions (for example, as AsO_4^{3-}, AsO_2^-). Therefore, it is proper to call them elements and not cations.

The Group V Oxyacids, Oxysalts, and Thiosalts

Oxyacids	Oxysalts	Thiosalts	Oxyacids	Oxysalts	Thiosalts
Meta-arsenous, $HAsO_2$	Sodium meta-arsenite, $NaAsO_2$	Sodium meta-thioarsenite, $NaAsS_2$	Ortho-antimonous, H_3SbO_3	Sodium ortho-antimonite, Na_3SbO_3	Sodium thioantimonite, Na_3SbS_3
Ortho-arsenous, H_3AsO_3	Sodium ortho-arsenite, Na_3AsO_3	Sodium thioarsenite, Na_3AsS_3	Meta-antimonic, $HSbO_3$	Sodium meta-antimonate, $NaSbO_3$	Sodium metathioantimonate, $NaSbS_3$
Meta-arsenic, $HAsO_3$	Sodium meta-arsenate, $NaAsO_3$	Sodium meta-thioarsenate, $NaAsS_3$	Ortho-antimonic, H_3SbO_4	Sodium ortho-antimonate, Na_3SbO_4	Sodium thioantimonate, Na_3SbS_4
Ortho-arsenic, H_3AsO_4	Sodium ortho-arsenate, Na_3AsO_4	Sodium thioarsenate, Na_3AsS_4	Stannous, H_2SnO_2	Sodium stannite, Na_2SnO_2	—
Meta-antimonous, $HSbO_2$	Sodium meta-antimonite, $NaSbO_2$	Sodium meta-thioantimonite, $NaSbS_2$	Meta-stannic, H_2SnO_3	Sodium stannate, Na_2SnO_3	Sodium thiostannate, Na_2SnS_3

The thioacid formed is immediately decomposed:

$$2H_3AsS_3 = As_2S_3 + 3H_2S$$

The Group V sulphides differ from each other in their solubility in acids, alkalies, and solutions of Na_2S, K_2S, $(NH_4)_2S$, and ammonium polysulphide.

The sulphides of arsenic, the properties of which are more acid than antimony and tin, dissolve not only in solutions of sulphides and polysulphides of alkali metals and ammonium, but also in ammonium carbonate, alkali hydroxides, and ammonia solution and do not dissolve in HCl, even in a concentrated solution.

The different solubility of the sulphides of arsenic, antimony, and tin in the above-mentioned reagents is used to separate arsenic from antimony and tin in the tests for Group V elements.

84. Group Reagent. Ammonium Polysulphide, $(NH_4)_2S_2$

To dissolve the Group V sulphides use is usually made of ammonium polysulphide which is obtained by shaking powdered sulphur with ammonium sulphide for a long time. The resulting solution contains a mixture of various sulphides: $(NH_4)_2S$, $(NH_4)_2S_2$, $(NH_4)_2S_3$, ... $(NH_4)_2S_9$. Consequently, the ammonium polysulphide solution contains S^{2-}, S_2^{2-}, S_3^{2-}, ... S_9^{2-} ions. The solution may also contain dissolved neutral sulphur. The formula for ammonium polysulphide is $(NH_4)_2S_2$ or $(NH_4)_2S_n$.

Ammonium polysulphide dissolves the sulphides of all the Group V elements, converting them to soluble thiosalts. The sulphides of the elements in their lower valency (As_2S_3, Sb_2S_3, SnS) are oxidized and give the same salts as are formed on dissolving the sulphides of higher valency:

$$Sb_2S_5 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + 3S$$

$$Sb_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S$$

Hence, ammonium polysulphide is an oxidizing agent.

85. Reactions of Group V Elements

The following form is recommended for tabulating the reactions of Group V elements:

Reagent	Ions					
	AsO_3^{3-}	AsO_4^{3-}	$SbCl_6^{3-}$	$SbCl_6^{-}$	$SnCl_4^{2-}$	$SnCl_6^{2-}$
Hydrogen sulphide, H_2S, in hydrochloric acid, HCl						
[To the precipitate formed by H_2S + HCl add, with heating:						
(a) Na_2S + NaOH						
(b) $(NH_4)_2S_2$						
(c) $(NH_4)_2CO_3$						
(d) concentrated HCl] . .						
[Treat the solution obtained on adding $(NH_4)_2S_2$ with HCl]						

1. Action of hydrogen sulphide on solutions of arsenites and arsenates. When hydrogen sulphide is passed into solutions of arsenites and arsenates no precipitate is produced because soluble thiosalts are formed:

$$Na_3AsO_3 + 3H_2S = Na_3AsS_3 + 3H_2O$$
$$AsO_3^{3-} + 3H_2S = AsS_3^{3-} + 3H_2O$$
$$Na_3AsO_4 + 4H_2S = Na_3AsS_4 + 4H_2O$$
$$AsO_4^{3-} + 4H_2S = AsS_4^{3-} + 4H_2O$$

A yellow flocky precipitate of arsenous sulphide is formed in hot solutions of arsenites containing hydrochloric acid of a concentration of 6 g-equiv per litre. Hydrogen sulphide precipitates arsenic sulphide from solutions of arsenates only at a concentration of hydrochloric acid of not less than 12 g-equiv per litre. In this case a precipitate is formed consisting of a mixture of arsenous and arsenic sulphides and yellow sulphur:

$$4Na_3AsO_4 + 10H_2S + 12HCl = As_2S_5\downarrow + As_2S_3\downarrow + 2S + 12NaCl + 16H_2O$$
$$O_4^{3-} + 10H_2S + 12H^+ = As_2S_5\downarrow + As_2S_3\downarrow + 2S + 16H_2O$$

Precipitation of As_2S_3 together with As_2S_5 is explained by the partial reduction of As^{5+} by hydrogen sulphide to As^{3+}:

$$Na_3AsO_4 + H_2S = Na_3AsO_3 + H_2O + S$$

$$AsO_4^{3-} + H_2S = AsO_3^{3-} + H_2O + S$$

Arsenous and arsenic sulphides dissolve in ammonium sulphide and polysulphide, alkali hydroxides, and in concentrated solutions of the carbonates of alkali metals and ammonium (unlike antimony and tin sulphides which do not dissolve in the carbonates of alkali metals and ammonium). Moreover, arsenous and arsenic sulphides dissolve in concentrated HNO_3 and do not dissolve in concentrated HCl (in contrast to antimony and tin sulphides which dissolve in concentrated HCl). The equations for the dissolution of arsenous and arsenic sulphides in alkali hydroxides are:

$$As_2S_3 + 6NaOH = Na_3AsS_3 + Na_3AsO_3 + 3H_2O$$

$$As_2S_3 + 6OH^- = AsS_3^{3-} + 3AsO_3^{3-} + 3H_2O$$

$$4As_2S_5 + 24NaOH = 5Na_3AsS_4 + 3Na_3AsO_4 + 12H_2O$$

$$4As_2S_5 + 24OH^- = 5AsS_4^{3-} + 3AsO_4^{3-} + 12H_2O$$

The equations for the dissolving of arsenous and arsenic sulphides in ammonium carbonate are:

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3CO_2$$

$$As_2S_5 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_4 + (NH_4)_3AsO_3 + S + 3CO_2$$

The equations for dissolving in ammonium polysulphide are:

$$As_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3AsS_4 + S$$

$$As_2S_5 + 3(NH_4)_2S_2 = 2(NH_4)_3AsS_4 + 3S$$

Arsenous and arsenic sulphides are precipitated by the action of an acid on the respective salt:

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 3H_2S + 6NH_4Cl$$

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 3H_2S + 6NH_4Cl$$

On dissolving arsenous and arsenic sulphides in concentrated HNO_3, arsenic is oxidized to the arsenate ion, AsO_4^{3-}, and sulphur to the sulphate ion, SO_4^{2-}.

The equation for the dissolving of As_2S_3 in HNO_3 is:

$$As_2S_3 + 28HNO_3 = 2H_3AsO_4 + 3H_2SO_4 + 28NO_2 + 8H_2O$$

$$1 \mid As_2S_3 + 20H_2O - 28e = 2AsO_4^{3-} + 3SO_4^{2-} + 40H^+$$

$$28 \mid HNO_3 + H^+ + e = NO_2 + H_2O$$

The equation for the dissolution of arsenic sulphide in HNO_3 is:

$$As_2S_5 + 40HNO_3 = 2H_3AsO_4 + 5H_2SO_4 + 40NO_2 + 12H_2O$$

$$1 \mid As_2S_5 + 28H_2O - 40e = 2AsO_4^{3-} + 5SO_4^{2-} + 56H^+$$

$$40 \mid HNO_3 + H^+ + e = NO_2 + H_2O$$

Procedure. Into a test tube containing 6-8 drops of 6*N* HCl solution (i.e., concentrated HCl diluted with water in a ratio of 1 : 1) introduce 3-5 drops of an arsenite solution. In another test tube place 8-10 drops of concentrated HCl and 3-5 drops of an arsenate solution. Heat the contents of each test tube to the boiling point and pass hydrogen sulphide into the boiling solution. A yellow precipitate will appear in both test tubes. Centrifuge and separate the precipitates from the supernatants. Wash the precipitates two or three times with hot water to free them from HCl, add 1-2 ml of water to each test tube, shake up their contents, and divide the mixture in each test tube into three portions. Treat the precipitates, with heating, as follows: one portion with $(NH_4)_2S_2$ solution; the second portion with $(NH_4)_2CO_3$ solution; the third portion with concentrated HNO_3 solution. The precipitates will be dissolved in all the test tubes.

To the solutions obtained after the action of ammonium polysulphide or ammonium carbonate add concentrated HCl solution a drop at a time until the mixture is acidic to litmus. Yellow precipitates of arsenous and arsenic sulphides will appear once more.

2. Action of hydrogen sulphide on solutions of antimonous and antimonic compounds. Hydrogen sulphide precipitates Sb_2S_3 and Sb_2S_5 (orange in colour) from 2*N* HCl solutions of antimonous and antimonic compounds[1]:

$$2[SbCl_6]^{3-} + 3H_2S = Sb_2S_3 + 6H^+ + 12Cl^-$$

$$2[SbCl_6]^- + 5H_2S = Sb_2S_5 + 10H^+ + 12Cl^-$$

Antimonous and antimonic sulphides dissolve in concentrated hydrochloric acid and in solutions of the sulphides and polysulphides of alkali metals and ammonium. In contrast to the sulphides of arsenic, Sb_2S_3 and Sb_2S_5 do not dissolve in ammonium carbonate solutions.

[1] Hydrochloric acid solutions of antimonous and antimonic chlorides mainly contain the complex ions, $[SbCl_6]^{3-}$ and $[SbCl_6]^-$.

The equations for the reactions of antimonous and antimonic sulphides with HCl are:

$$Sb_2S_3 + 12HCl = 2H_3[SbCl_6] + 3H_2S$$
$$Sb_2S_5 + 12HCl = 2H[SbCl_6] + 5H_2S$$

The equations for the reaction of Sb_2S_3 with ammonium sulphide are:

$$Sb_2S_3 + (NH_4)_2S = 2(NH_4)SbS_2$$
$$Sb_2S_3 + S^{2-} = 2SbS_2^-$$

The equations for the reaction of Sb_2S_3 with ammonium polysulphide are:

$$Sb_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S$$
$$Sb_2S_3 + 3S_2^{2-} = 2SbS_4^{3-} + S$$

On treating thioantimonites and thioantimonates with 2*N* HCl solution, an orange precipitate is formed:

$$2NH_4SbS_2 + 2HCl = Sb_2S_3 + 2NH_4Cl + H_2S$$
$$2SbS_2^- + 2H^+ = Sb_2S_3 + H_2S$$
$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S$$
$$2SbS_4^{3-} + 6H^+ = Sb_2S_5 + 3H_2S$$

Procedure. Place in separate test tubes solutions of antimonous and antimonic ions. To each test tube add 2 or 3 drops of 2*N* HCl solution. Pass hydrogen sulphide into the solutions. Orange precipitates of the sulphides will be formed in both test tubes. Divide each precipitate into two portions and, heating them, to one portion add concentrated HCl solution; to the other portion, ammonium polysulphide or alkaline solution of Na_2S or K_2S. The precipitates will be dissolved. Add 2*N* HCl solution to each test tube until the solutions are acidic; Sb_2S_3 and Sb_2S_5, orange in colour, will be precipitated once more.

3. Action of hydrogen sulphide on solutions of stannous and stannic compounds. Hydrogen sulphide in a 2*N* hydrochloric acid solution of stannous or stannic compounds [1] precipitates, respectively, the chocolate-coloured SnS or the yellow SnS_2. Both precipitates dissolve, on heating, in con-

[1] Hydrochloric acid solutions of stannous and stannic chloride mainly contain the complex ions, $[SnCl_4]^{2-}$ and $[SnCl_6]^{2-}$.

centrated HCl solutions and in ammonium polysulphide solutions. Stannic sulphide, SnS_2, is also dissolved in ammonium sulphide solutions and in solutions of sulphides of the alkali metals, whereas stannous sulphide, SnS, is not dissolved in $(NH_4)_2S$ nor in an alkaline solution of K_2S or Na_2S.

The equations for the reaction of SnS and SnS_2 with concentrated HCl solutions are:

$$SnS + 4HCl = H_2[SnCl_4] + H_2S$$
$$SnS_2 + 6HCl = H_2[SnCl_6] + 2H_2S$$

The equation for the reaction of SnS_2 with ammonium sulphide is

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

When ammonium polysulphide reacts with SnS, the latter is first oxidized to SnS_2, then SnS_2 is dissolved in $(NH_4)_2S_2$ with the formation of ammonium thiostannate. The equations for the reactions are:

$$SnS + (NH_4)_2S_2 = SnS_2 + (NH_4)_2S$$
$$SnS + S_2^{2-} = SnS_2 + S^{2-}$$
$$SnS_2 + (NH_4)_2S_2 = (NH_4)_2SnS_3 + S$$
$$SnS_2 + S_2^{2-} = SnS_3^{2-} + S$$

In an acidic solution the yellow precipitate of stannic sulphide, SnS_2, is formed:

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + SnS_2 + H_2S$$
$$SnS_3^{2-} + 2H^+ = SnS_2 + H_2S$$

Procedure. Place in separate test tubes 2 or 3 drops of solutions of a stannous and stannic compound. To each of them add 2 or 3 drops of 2*N* HCl solution and pass H_2S into the mixtures. Chocolate-coloured SnS and yellow SnS_2 will be precipitated. Divide each precipitate into two portions. Add concentrated HCl solution to one of the portions; the precipitate will be dissolved. Add $(NH_4)_2S_2$ solution to the other portion; the precipitate will be dissolved as the result of the formation of ammonium thiostannate. To the resultant solutions of the thiosalts add 2*N* HCl until the solution is acidic; a yellow precipitate, SnS_2, will appear in both test tubes.

86. Arsenic. Tests for Arsenous Ion, As^{3+}, and Arsenic Ion, As^{5+}

In aqueous solution arsenic is usually found in the anion. However, the analytical chemistry of arsenic is always included in the section of analytical chemistry that deals with cations because the arsenites and arsenates react with hydrogen sulphide in a hydrochloric acid solution to form the sulphides As_2S_3 and As_2S_5 which are precipitated together with the sulphides of Groups IV and V.

Arsenic forms two oxides: As_2O_3, arsenous oxide, and As_2O_5, arsenic oxide. These oxides are anhydrides of arsenous and arsenic acids, respectively.

1. Hydrogen sulphide in strong hydrochloric acid solutions precipitates yellow arsenous and arsenic sulphides which dissolve in concentrated ammonium carbonate solution.

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of 6*N* HCl solution. Heat the mixture to boiling and pass H_2S into it. Centrifuge and remove the supernatant with a dropper pipette; treat the precipitate (with heating) with concentrated $(NH_4)_2CO_3$ solution. Then centrifuge once more, separate the precipitate from the supernatant and add 2*N* HCl solution to the clear supernatant until the solution is acidic. The presence of arsenic is indicated by the appearance of a yellow precipitate.

2. Silver nitrate precipitates from neutral solutions of arsenites and arsenates silver arsenite, Ag_3AsO_3, yellow in colour, and silver arsenate, $AgAsO_4$, of a chocolate-brown colour. Both precipitates are dissolved in ammonia solution and in nitric acid. The equations for the dissolving of silver arsenite and silver arsenate in ammonia solution are:

$$Ag_3AsO_3 + 6NH_4OH = [Ag(NH_3)_2]_3AsO_3 + 6H_2O$$
$$Ag_3AsO_3 + 6NH_4OH = 3[Ag(NH_3)_2]^+ + AsO_3^{3-} + 6H_2O$$
$$Ag_3AsO_4 + 6NH_4OH = [Ag(NH_3)_2]_3AsO_4 + 6H_2O$$
$$Ag_3AsO_4 + 6NH_4OH = 3[Ag(NH_3)_2]^+ + AsO_4^{3-} + 6H_2O$$

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of 0.1*N* $AgNO_3$ solution. A yellow precipitate indicates the presence of As^{3+}; a chocolate-coloured preci-

pitate, the presence of As^{5+}. Treat both precipitates with ammonia solution; they will be dissolved.

3. Magnesia mixture (a mixture of magnesium chloride, ammonium chloride, and ammonia solution) forms with arsenates a white crystalline precipitate, $MgNH_4AsO_4$. Arsenites do not react in this way.

Procedure. To 3-5 drops of magnesium chloride solution add $2N$ ammonia solution until a precipitate appears, then $2N$ NH_4Cl solution until the precipitate is dissolved. To the magnesia mixture thus obtained add 3-5 drops of the solution under test, shake, and rub a glass rod against the walls of the test tube. In the presence of AsO_4^{3-} a white crystalline precipitate will appear. The presence of PO_4^{3-} ions interferes with this test.

4. Ammonium molybdate in nitric acid solutions of arsenates forms a precipitate of $(NH_4)_3AsMo_{12}O_{40}$ which is yellow in colour:

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 =$$
$$= (NH_4)_3AsMo_{12}O_{40} + 21NH_4NO_3 + 12H_2O$$

The precipitate is formed only if there is a large excess of ammonium molybdate.

Procedure. To 2 or 3 drops of the solution under test add 5 or 6 drops of HNO_3 solution (density 1.2) and 7 or 8 drops of a nitric acid solution of $(NH_4)_2MoO_4$. Boil the mixture. A yellow precipitate will appear in the presence of As^{5+}. The presence of PO_4^{3-} ions interferes with the detection of arsenic because PO_4^{3-} ions, under these conditions, precipitate ammonium phosphomolybdate which is also of a yellow colour.

87. Antimony. Tests for Antimonous Ion, Sb^{3+}, and Antimonic Ion, Sb^{5+}

Antimony forms antimonous and antimonic compounds in which it is trivalent and pentavalent, respectively.

Antimonous and antimonic chlorides in an excess of HCl form the complex hexachloroantimonous acid, $H_3[SbCl_6]$, and hexachloroantimonic acid, $H[SbCl_6]$:

$$SbCl_3 + 3HCl = H_3[SbCl_6]$$
$$SbCl_5 + HCl = H[SbCl_6]$$

As can be seen from the equations, a hydrochloric acid solution of antimonous chloride contains the complex hexachloroantimonite ion, $[SbCl_6]^{3-}$, and that of antimonic chloride, the hexachloroantimonate ion, $[SbCl_6]^-$.

The antimony sulphides Sb_2S_3 and Sb_2S_5 dissolve in concentrated hydrochloric acid and also in solutions of the sulphides and polysulphides of alkali metals and ammonium with which they form thiosalts, for example, $Na_3[SbS_3]$ and $Na_3[SbS_4]$.

1. Hydrogen sulphide in weak hydrochloric acid solutions precipitates Sb^{3+} and Sb^{5+} in the form of Sb_2S_3 and Sb_2S_5, orange in colour.

2. Zinc, aluminium, magnesium, iron, and other metals which precede antimony in the electromotive series reduce antimony compounds in an acidic solution to metallic antimony:

$$2H_3SbCl_6 + 3Mg = 2Sb\downarrow + 3MgCl_2 + 6HCl$$

$$2[SbCl_6]^{3-} + 3Mg = 2Sb\downarrow + 3Mg^{2+} + 12Cl^-$$

Procedure. In a test tube containing 0.5 ml of the solution under test place a small piece of magnesium or iron, add 5-8 drops of concentrated HCl solution and boil the mixture for 2-3 minutes. Black flakes will appear in the presence of antimony.

88. Tin. Tests for Stannous Ion, Sn^{2+}, and Stannic Ion, Sn^{4+}

Tin forms stannous and stannic compounds in which it is bivalent and tetravalent, respectively. Hydrochloric acid solutions of stannous and stannic chlorides chiefly contain the complex chlorostannite ion, $[SnCl_4]^{2-}$, and chlorostannate ion, $[SnCl_6]^{2-}$.

1. Mercuric chloride forms a white precipitate of calomel, Hg_2Cl_2, with stannous compounds. The precipitate grows black in the presence of excess Sn^{2+} ions because metallic mercury is precipitated:

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4$$

$$SnCl_2 + Hg_2Cl_2 = 2Hg + SnCl_4$$

or

$$H_2[SnCl_4] + 2HgCl_2 = Hg_2Cl_2\downarrow + H_2[SnCl_6]$$
$$H_2[SnCl_4] + Hg_2Cl_2 = 2Hg\downarrow + H_2[SnCl_6]$$

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of $HgCl_2$ solution. The appearance of a white precipitate that gradually turns grey and then black indicates the presence of Sn^{2+}.

2. Bismuth salts in an alkaline solution are reduced by stannites to metallic bismuth which appears as a black precipitate (see Sec. 80):

$$3SnO_2^{2-} + 2Bi^{3+} + 6OH^- = 3SnO_3^{2-} + 2Bi + 3H_2O$$

3. Metallic iron reduces stannic to stannous ions but not to metallic tin:

$$H_2[SnCl_6] + Fe = H_2SnCl_4 + FeCl_2$$
$$[SnCl_6]^{2-} + Fe = [SnCl_4]^{2-} + 2Cl^-$$

Procedure. In a test tube containing 5-8 drops of the solution under test place a small piece of iron or a steel pin and add 5-8 drops of 6*N* HCl solution. Heat the solution for 2-3 minutes and add 2 or 3 drops of $HgCl_2$ solution into the test tube. In the presence of tin a white, grey, or black precipitate (a mixture of Hg_2Cl_2 and metallic Hg) will appear.

4. Magnesium and zinc reduce Sn^{4+} to metallic tin:

$$H_2[SnCl_6] + 2Mg = Sn + 2MgCl_2 + 2HCl$$
$$[SnCl_6]^{2-} + 2Mg = Sn + 2Mg^{2+} + 6Cl^-$$

89. Analysis of Mixture of Group V Elements

The separation of a mixture of Group V elements is based on the solubility of arsenous and arsenic sulphides in ammonium carbonate solution and their insolubility in concentrated HCl solution, on the one hand, and the insolubility of the sulphides of tin and antimony in ammonium carbonate solution and their solubility in concentrated HCl solution, on the other hand. A mixture of tin and antimony compounds can be separated with the aid of metallic iron which reduces stannic ions to stannous ions. Therefore, tin remains in solution as stannous compounds, while antimony is isolated as the metal.

The analysis of a mixture of compounds of Group V elements is conducted in accordance with the following scheme:

1. Precipitation of sulphides. To 3-4 ml of the neutral solution under test add not more than 2 or 3 drops of concentrated HCl solution, heat the solution to boiling and, without allowing it to cool, pass hydrogen sulphide into it for 2-3 minutes. Add an equal volume of distilled water or hydrogen-sulphide water and pass H_2S into the cold mixture for 2-3 minutes. Centrifuge. Check for completeness of precipitation by passing hydrogen sulphide into the clear supernatant; the solution should not become turbid.

If a precipitate or turbidity appears, add another 1-2 ml of distilled water and pass H_2S into the mixture once more. Only after making sure that precipitation of the Group V sulphides is complete, separate the solution from the precipitate. An orange precipitate indicates the presence of antimonous and antimonic sulphides; a yellow precipitate, arsenous, arsenic, and stannic sulphides; a chocolate-coloured precipitate, stannous sulphide. A milk-white precipitate is usually sulphur; its precipitation indicates the absence of Group V elements in the solution under test.

Separate coloured precipitate 1 from supernatant 1.

Precipitate 1: Group V sulphides; analyze as described in *P* 2.

Supernatant 1: excess hydrochloric acid; is not analyzed.

2. Separation of sulphides of arsenic from sulphides of antimony and tin. Wash precipitate 1 with hot water and transfer to an evaporating dish, add 2-3 ml of concentrated $(NH_4)_2CO_3$ solution and heat for 2-3 minutes over a small flame, stirring constantly. Then centrifuge the mixture and separate precipitate 2 from supernatant 2.

Precipitate 2: sulphides of antimony and tin; analyze as described in *P* 4.

Supernatant 2: thiosalts of arsenic; analyze as described in *P* 3.

3. Precipitation of sulphides of arsenic. To supernatant 2 carefully add concentrated HCl solution drop by drop until the solution is acidic to litmus. The appearance of a yellow precipitate indicates the presence of arsenic.

4. Dissolving of sulphides of antimony and tin. Wash the precipitate with hot water, transfer it to an evaporating

dish, and add 1-2 ml of concentrated HCl solution. Heat the mixture for 1-2 minutes over a small flame, stirring constantly. Centrifuge the suspension, discard the precipitate and test for antimony and tin in the supernatant.

5. Separation of antimony from tin. Place a small piece of magnesium in the hydrochloric solution obtained above. Antimony will be reduced to the metal, which is indicated by the precipitation of black flakes; tin is also reduced to the metal, but unlike antimony, it is dissolved in concentrated HCl solution. Therefore, add 1 ml of concentrated HCl solution to the mixture, heat it to boiling, add 1 ml of distilled water, centrifuge the mixture, and separate precipitate 3 from supernatant 3.

Precipitate 3: metallic antimony; analyze as described in *P* 6.

Supernatant 3: stannous chloride; analyze as described in *P* 7.

6. Confirmatory test for antimony. Wash precipitate 3 with hot water, transfer to an evaporating dish and dissolve it, with boiling, in a mixture of 1 ml of 2*N* HCl solution and 0.5 ml of 3 per cent H_2O_2 solution. Boil the solution to complete decomposition of H_2O_2 (until effervescence ceases) and pass H_2S into it. The appearance of an orange precipitate confirms the presence of antimony.

7. Test for tin. To supernatant 3 add $HgCl_2$ solution. The appearance of a white, grey, or black precipitate confirms the presence of tin.

Review Questions

1. How do the analytical properties of Group V cations differ from those of Group IV cations?
2. How are Group V elements separated from Group IV cations?
3. What is the composition and properties of ammonium polysulphide?
4. What compounds are called thiosalts (or sulphosalts)?
5. How is a soluble thiosalt converted to a sulphide?
6. Write the equation for the dissolving of SnS in $(NH_4)_2S_2$.
7. How do the properties of the sulphides of arsenic differ from the properties of the sulphides of antimony and tin?
8. What are the terms for the salts of arsenic, antimonic, and stannic acids?

90. Analysis of Mixture of Elements of Groups IV and V

The analysis of a mixture of elements of Groups IV and V is begun by separating the elements of the silver subgroup of Group IV. On treating the mixture with hydrochloric acid, the chlorides of the silver subgroup are precipitated, namely, AgCl, Hg_2Cl_2, and $PbCl_2$.

Group V elements and the copper subgroup of Group IV are precipitated from hydrochloric acid solutions as sulphides. It should be taken into account that all the sulphides of the copper subgroup and Group V elements, with the exception of arsenic sulphide, are completely precipitated from 0.3*N* HCl solution. Arsenic sulphide, As_2S_5, under these conditions is either incompletely precipitated or not precipitated at all. However, it is readily precipitated from hot hydrochloric acid solution of a concentration of approximately 12*N*. Therefore, hydrogen sulphide should first be passed into hot strongly acidic solutions in order to precipitate As_2S_5 and then the mixture should be considerably diluted with water and the cold solution saturated once more with hydrogen sulphide in order to precipitate the rest of the sulphides.

The separation of Group V elements from those of the copper subgroup is based on the formation of soluble thiosalts of the alkali metals and ammonium by the Group V elements. Separation is achieved by treating the mixture of sulphides of both groups with ammonium polysulphide or alkaline solution of K_2S or Na_2S. When treating the mixture with ammonium polysulphide, it must be borne in mind that CuS is appreciably soluble in $(NH_4)_2S_2$ and copper therefore partly passes into the solution together with the Group V thiosalts. When using alkaline solution of K_2S or Na_2S, mercuric sulphide forms a complex compound that is soluble in water. Consequently, mercury passes into the solution together with the Group V elements. If an alkaline solution of K_2S or Na_2S is used, it is necessary to first oxidize Sn^{2+} to Sn^{4+} because SnS_2 dissolves in the alkaline solution, whereas SnS does not.

The analysis of a mixture of compounds of elements of Groups IV and V is conducted in the following sequence:

1. Preliminary tests. A blue solution indicates the presence of Cu^{2+} salts.

2. Precipitation of elements of the silver subgroup as chlorides. To 8-10 ml of the solution under test heated to the boiling point, add 2*N* HCl solution drop by drop until precipitation is complete (see Sec. 73, *P* 1). To test for completeness of precipitation heat the mixture to boiling, allow to cool, centrifuge, and add a few drops of 2*N* HCl solution to the centrifugate. The solution should not become turbid. On making sure that precipitation is complete, separate precipitate 1 from supernatant 1.

Precipitate 1: chlorides of the silver subgroup AgCl, Hg_2Cl_2, $PbCl_2$; analyze as described in the systematic scheme of analysis in Sec. 73, *P* 2 to *P* 5.

Supernatant 1: cations of the copper subgroup and Group V elements; analyze as described in *P* 3.

3. Precipitation of sulphides of the copper subgroup and sulphides of Group V elements. To supernatant 1 add concentrated ammonium solution a drop at a time until the solution is weakly alkaline to litmus. Pay no attention to the appearance of a precipitate. Then add 2*N* HCl solution drop by drop until the solution is slightly acidic (any precipitate that has formed should dissolve). Add to the slightly acidic solution obtained above 3-5 drops of 3 per cent H_2O_2 solution to convert Sn^{2+} to Sn^{4+} (stannous sulphide is insoluble in K_2S or Na_2S). Heat the mixture in a water bath to complete decomposition of H_2O_2 (until small bubbles are no longer evolved). Then add not more than 2 or 3 drops of concentrated HCl solution. Heat the mixture to boiling and into the hot solution pass hydrogen sulphide during 2-3 minutes. Add to the solution an equal volume of distilled water or hydrogen-sulphide water and again pass hydrogen sulphide into the mixture during 2-3 minutes. Check for completeness of precipitation by centrifuging the mixture and passing H_2S into the clear solution. The solution should not become turbid. If a precipitate or suspended matter appears, add another 1-2 ml of distilled water or hydrogen-sulphide water and pass hydrogen sulphide into the solution once more. Only after making sure that precipitation is complete, separate precipitate 2 from supernatant 2.

Precipitate 2: sulphides of the copper subgroup and Group V elements; analyze as described in *P* 4 et seq.

Supernatant 2: solution of cations of Groups I, II, and III (if present); analyze as described in the systematic scheme of analysis given in Sec. 62.

4. Separation of Group V elements from those of the copper subgroup. Precipitate 2 may be yellow, orange, or black. A yellow or orange colour indicates the presence of elements of Group V and of cadmium; a black colour indicates the presence of Group IV elements and, possibly, Group V elements. Whatever the colour of the precipitate may be, wash it 2 or 3 times with NH_4Cl solution saturated with hydrogen sulphide (dissolve 10 g of NH_4Cl in 100 ml of water and pass hydrogen sulphide into the solution during several minutes). Transfer the washed precipitate to an evaporating dish and add to it 5-10 ml of alkaline K_2S or Na_2S solution (dissolve 48 g of Na_2S or 70 g of K_2S and 4 g of NaOH in 100 ml of water). Heat the mixture in the dish over a small flame at a temperature of 50-60° C (but not to boiling) or, what is even better, in a hot water bath, and keep it at this temperature for 3-4 minutes, strirring from time to time with a glass rod. Allow the residue to settle and carefully transfer the solution with a dropper pipette to a beaker or flask. Treat the residue in the dish a second time with 5-6 ml of alkaline K_2S or Na_2S solution under the same conditions as described above. Centrifuge the mixture and decant the clear liquid (supernatant 3) into the same beaker or flask into which the solution obtained after the first treatment of the residue (residue 3) was transferred.

Residue 3: sulphides of lead, bismuth, copper, and cadmium; analyze as described in *P* 5.

Supernatant 3: thiosalts of arsenic, antimony, and tin, and the complex mercury salt; analyze as described in *P* 6.

5. Dissolving of sulphides of the copper subgroup. Wash residue 3 with hot water containing NH_4Cl, transfer to an evaporating dish, add to it 3-5 ml of 2*N* HNO_3 solution and 0.5 ml of 2*N* $NaNO_2$ or KNO_2 solution. Boil the mixture until the precipitate is completely dissolved and test for Pb^{2+}, Cu^{2+}, Cd^{2+}, and Bi^{3+} ions in the solution (see Sec. 81, *P* 8 to *P* 12).

6. Precipitation of sulphides of Group V and mercury. Add to supernatant 3 concentrated acetic acid a drop at a time until the solution is acidic to litmus. A yellow or orange colour of the precipitate indicates the presence of Group V sulphides; a black colour, mercuric sulphide and, possibly, Group V sulphides. If a milk-white precipitate (sulphur) appears, it may be concluded that the sulphides of Group V and mercury are absent. Add acetic acid to the mixture until the solution is acidic, boil it for 1-2 minutes, and centrifuge.

Precipitate 4: the sulphides of elements of Group V and mercury; analyze as described in *P* 7 et seq.

Supernatant 4: is not analyzed.

7. Separation of antimony and tin from arsenic and mercury. Wash precipitate 4 with hot water, transfer to an evaporating dish, add to it 3-5 ml of concentrated HCl solution, heat the mixture to boiling and, stirring constantly, boil for 2-3 minutes (under a draft hood). Add to the mixture 3-5 ml of distilled water, centrifuge, and separate residue 5 from supernatant 5.

Residue 5: sulphides of arsenic and mercury; analyze as described in *P* 8.

Supernatant 5: soluble salts of antimony and tin, for example, $Na[SbCl_6]$, $Na_3[SbCl_6]$, and $Na_2[SnCl_6]$; analyze as described in the systematic scheme of analysis given in Sec. 89, *P* 5, *P* 7.

8. Separation of arsenic from mercury. Wash residue 5 with hot water, transfer to an evaporating dish, add to it 1-2 ml of distilled water and 3 or 4 small crystals of $(NH_4)_2CO_3$, and heat the mixture over a small flame for 1-2 minutes. The sulphides of arsenic will be dissolved, whereas mercuric sulphide will remain undissolved. Centrifuge and separate residue 6 (mercuric sulphide) from supernatant 6 (thiosalt of arsenic).

Residue 6: mercuric sulphide; analyze as described in *P* 9.

Supernatant 6: thiosalt of arsenic; analyze as described in *P* 10.

9. Test for mercury. Wash residue 6 with hot water, transfer to an evaporating dish, add to it 1-2 ml of concentrated HCl and 1 ml of 3 per cent H_2O_2 solution. Heat the mixture in a boiling water bath until the black particles

disappear and H_2O_2 is completely decomposed. Then add a clear solution of $SnCl_2$. The appearance of a white, grey, or black precipitate indicates the presence of mercury.

10. Test for arsenic. To supernatant 6 add concentrated HCl solution carefully drop by drop to make it acidic (until CO_2 is no longer liberated). The appearance of a coloured precipitate indicates the presence of arsenic.

91. Analysis of Mixture of Elements of Groups I, II, III, IV, and V

1. Preliminary observations and tests: (a) by the colour of the solution ascertain approximately the presence or absence of elements whose salts are coloured: Cu^{2+} (see Sec. 90, *P* 1), Ni^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+} (see Sec. 62 preceding *P* 1); (b) determine the pH of the solution by means of indicator paper; (c) in separate portions of the solution, by the method of separation or isolation, test for Fe^{3+}, Fe^{2+}, Cr^{3+}, Mn^{2+}, and NH_4^+ ions (see Sec. 62, *P* 2).

2. Precipitation of chlorides of silver subgroup. Stir the mixture under test thoroughly, transfer 4-5 ml of the mixture to a small flask, heat to boiling and add 2*N* HCl solution drop by drop to complete precipitation (see Sec. 73, *P* 1). Centrifuge the mixture and separate precipitate 1 from supernatant 1.

Precipitate 1: chlorides of the silver subgroup and, possibly, sulphates of lead and the alkaline earth metals and basic salts of bismuth, antimony, and tin; analyze as described in *P* 3.

Supernatant 1: salts of elements of all the groups besides the silver subgroup; analyze as described in *P* 4 et seq.

3. Analysis of precipitate 1. Wash precipitate 1 with 2*N* HCl solution and add the wash water to supernatant 1. Transfer the precipitate to an evaporating dish and add to it 2-3 ml of water. Heat the mixture to boiling, quickly centrifuge and test the supernatant for the presence of lead (see Sec. 73, *P* 3). Treat the residue (obtained after treating with hot water) with 1 ml of concentrated ammonia solution. Stir the mixture thoroughly and centrifuge. Mercurous

ions are indicated if the residue turns black. Test for silver in the ammoniacal solution obtained above (see Sec. 73, *P* 5). To detect lead ions and those of the alkaline earth metals, transfer the residue (obtained after treating with the ammonia solution) to an evaporating dish, add to it 5 or 6 drops of bromine water [1] and boil the mixture until the black particles disappear and excess bromine is removed. Centrifuge the mixture, discard the supernatant and transfer the residue to an evaporating dish, add to it 1-2 ml of 6*N* NaOH solution, heat to boiling, boil for 1-2 minutes and centrifuge. Acidify the resulting supernatant with acetic acid.

The appearance of a precipitate indicates the presence of lead ions. Boil the residue (obtained after treating with NaOH solution) containing sulphates of the alkaline earth metals with a mixture of Na_2CO_3 and K_2CO_3 (see Sec. 38, *P* 7) and test as described in the scheme given in Sec. 37.

4. Separation of elements of Groups IV and V from the cations of Groups I, II, and III. Neutralize supernatant 1 with ammonia solution until it is slightly acidic and add 2 or 3 drops of 3 per cent H_2O_2 solution. Boil the mixture to complete decomposition of hydrogen peroxide, add 1 or 2 drops of concentrated HCl, heat to boiling, and pass hydrogen sulphide into it (see Sec. 90, *P* 7). Then dilute the mixture with water and pass hydrogen sulphide into the cold mixture. Centrifuge, make sure that precipitation is complete and separate precipitate 2 from supernatant 2. A black precipitate indicates the presence of at least one of the following sulphides: HgS, PbS, Bi_2S_3, CuS; a yellow precipitate: CdS, As_2S_3, SnS_2; an orange-red precipitate: Sb_2S_3, Sb_2S_5.

Precipitate 2: sulphides of Groups IV and V; analyze as described in the scheme given in Sec. 90.

Supernatant 2: cations of Groups I, II, and III; analyze as described in the scheme given in Sec. 62.

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[1] The precipitate is treated with bromine water only when mercury ions are present, which is indicated by the black colour of the precipitate.

ANIONS

CHAPTER XVIII

Analytical Classification of the Anions

92. Anion Groups

There is no generally accepted analytical classification of the anions at present. The classification given in this textbook is based on the different reactions of the anions with two reagents: $AgNO_3$ and $BaCl_2$. With respect to these reagents, the anions are divided into three groups.

Analytical Classification of the More Commonly Encountered Anions

Group	Group characteristics	Anions
I	With $AgNO_3$ a precipitate insoluble in HNO_3 is formed With $BaCl_2$ no precipitate is formed	Chloride, Cl^-; bromide, Br^-, Iodide, I^-; sulphide, S^{2-}
II	With $AgNO_3$ a precipitate soluble in HNO_3* is formed With $BaCl_2$ a precipitate soluble in HNO_3* is formed	Carbonate, CO_3^{2-}; borate, BO_3^{3-}; sulphate, SO_4^{2-}, sulphite, SO_3^{2-}; thiosulphate, $S_2O_3^{2-}$; arsenite AsO_3^{3-}; arsenate, AsO_4^{3-}; phosphate, PO_4^{3-}; chromate, CrO_4^{2-}; silicate, SiO_3^{2-}
III	With $AgNO_3$ and $BaCl_2$ no precipitate is formed	Nitrate, NO_3^-; nitrite, NO_2^-

* The sulphate ion, SO_4^{2-}, is an exception in Group II. It forms a precipitate with $AgNO_3$ only in concentrated solutions; with $BaCl_2$ it produces a precipitate that is insoluble in HNO_3.

CHAPTER XIX

Group I Anions

(Cl^-, Br^-, I^-, S^{2-})

Salts containing Group I anions form precipitates of silver salts that are insoluble in HNO_3. They do not form any precipitate with $BaCl_2$.

Group I is made up of the anions of the following acids: hydrochloric, hydrobromic, hydriodic, and hydrosulphuric.

93. Reactions of Group I Anions

It is recommended that solutions of NaCl or KCl, NaBr or KBr, NaI or KI, Na_2S or K_2S or hydrogen-sulphide water be used for studying the reactions of Group I anions.

1. Silver nitrate with salts containing the Cl^- ion produces a white curdy precipitate of silver chloride, AgCl; the Br^- ion, a pale yellow precipitate of silver bromide, AgBr; the I^- ion, a yellow curdy precipitate of silver iodide, AgI; the S^{2-} ion, a black precipitate of silver sulphide, Ag_2S.

All these precipitates are insoluble in nitric acid. Silver chloride is readily dissolved in ammonia solution and in 10 per cent ammonium carbonate solution:

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$$

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

$$2AgCl + 3(NH_4)_2CO_3 = [Ag(NH_3)_2]_2CO_3 + 2H_2O + 2NH_4Cl + 2CO_2$$

If a mineral acid is added to the resulting ammoniacal solution of silver chloride, AgCl will be precipitated once more as a result of decomposition of the complex ion $[Ag(NH_3)_2]^+$:

$$[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl + 2NH_4NO_3$$

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ = AgCl + 2NH_4^+$$

Silver bromide is sparingly soluble in ammonia solution and does not dissolve in ammonium carbonate. Silver iodide and silver sulphide do not dissolve in ammonia solution or in ammonium carbonate.

Procedure. Place in four test tubes 2 or 3 drops of solutions of NaCl, NaBr, NaI, and Na_2S (or KCl, KBr, KI, and K_2S) and add 2 or 3 drops of 0.1 *N* $AgNO_3$ solution to each test tube. Record the colour of each precipitate formed in your notebook. Treat the precipitates with ammonia solution. AgCl is readily soluble in NH_4OH; AgBr, difficultly soluble; AgI and Ag_2S do not dissolve at all. To the ammoniacal solutions obtained above add 2*N* HNO_3 to make the solution acidic; AgCl and AgBr will be reprecipitated.

2. Lead acetate or lead nitrate forms precipitates with solutions of salts containing Cl^-, Br^-, I^-, and S^{2-} ions, namely: the white precipitates of $PbCl_2$ and $PbBr_2$, the yellow precipitate of PbI_2, the black precipitate of PbS. The halides of lead are soluble in hot water; on cooling the solutions, they are reprecipitated.

Procedure. To solutions of NaCl, NaBr, NaI, and Na_2S, contained in separate test tubes, add 2 or 3 drops of lead acetate or lead nitrate. Make a note of the colour of each precipitate formed. To each test tube add 2 or 3 drops of water and heat the mixture. The precipitates of $PbCl_2$, $PbBr_2$, and PbI_2 will be dissolved. Allow the solution to cool slowly. Crystalline precipitates will appear again.

94. Test for Chloride Ion, Cl^-

The Cl^- ion is the anion of hydrochloric acid. Hydrochloric acid is one of the strongest acids. It forms salts called chlorides. All the chlorides are water-soluble except AgCl, Hg_2Cl_2, $PbCl_2$, CuCl, and the basic chlorides (subchlorides) of bismuth and antimony, BiOCl and SbOCl. The Cl^- ion is colourless.

Silver nitrate in a nitric acid solution produces with chloride solutions a white curdy precipitate that is soluble in ammonia solution and in 10 per cent ammonium carbonate solution. On adding nitric acid to the ammoniacal solution of silver chloride, a white precipitate of AgCl will be reprecipitated.

Procedure. To 2 or 3 drops of the solution under test add 2 or 3 drops of 0.1*N* $AgNO_3$ solution. Centrifuge and remove the clear liquid with the aid of a dropper pipette. Treat the precipitate with 2 or 3 drops of 10 per cent $(NH_4)_2CO_3$ solu-

tion or 2*N* NH_4OH solution. Stir the mixture thoroughly. If the precipitate is not completely dissolved, centrifuge. To the clear ammoniacal solution obtained add 2*N* HNO_3 solution until the solution is acidic to litmus. In the presence of Cl^- ions a precipitate or suspended matter will appear.

95. Test for Bromide Ion, Br^-

The Br^- ion is the anion of hydrobromic acid, HBr (an aqueous solution of hydrogen bromide). Hydrobromic acid forms salts called bromides. Their solubility is similar to that of chlorides: all of them, with the exception of AgBr, $PbBr_2$, Hg_2Br_2, and CuBr, are soluble in water. The Br^- ion is colourless.

Chlorine water (an aqueous solution of chlorine) oxidizes the bromine ion to free bromine:

$$2NaBr + Cl_2 = Br_2 + 2NaCl$$

$$2Br^- + Cl_2 = Br_2 + 2Cl^-$$

Free bromine on dissolving in organic solvents such as benzene, carbon disulphide, and chloroform, imparts a straw-yellow colour to the solution. When excess chlorine water is added to these solutions, the coloration disappears because bromic acid, $HBrO_3$, is formed.

Procedure. To 1 or 2 drops of the solution under test add 2 or 3 drops of 2*N* H_2SO_4 solution and 0.5 ml of benzene or any other organic solvent immiscible with water. Add chlorine water to the mixture drop by drop, stirring thoroughly after adding each drop. In the presence of bromide ions, the layer of organic solvent will first be coloured straw-yellow and, on adding more chlorine water, will be decolourized.

96. Tests for Iodide Ion, I^-

The I^- ion is the anion of hydriodic acid, HI (an aqueous solution of hydrogen iodide). Hydriodic acid is a strong acid and a strong oxidizing agent. It forms salts called iodides, all of which, with the exception of AgI, Hg_2I_2, PbI_2, BiI_3, and CuI are soluble in water. The I^- ion is colourless.

1. Chlorine water oxidizes iodide ions to elementary iodine:

$$2I^- + Cl_2 = I_2 + 2HCl$$
$$2I^- + Cl_2 = I_2 + 2Cl^-$$

The liberated iodine can be detected with the aid of starch solution (by the blue colour produced) or by shaking the solution under test with an organic solvent which in the presence of I_2 assumes a red-violet colour.

Procedure. (a) To a drop of the solution under test add 0.5 ml of starch solution and 1 or 2 drops of chlorine water. Shake the mixture. In the presence of iodide ions, the solution will turn blue. (b) To one drop of the solution under test add 0.5 ml of $2N$ H_2SO_4 solution, 0.5 ml of benzene (or any other organic solvent) and 2 or 3 drops of chlorine water. Shake the mixture vigorously and allow it to settle. In the presence of iodide ions, the layer of organic solvent will assume a red-violet colour. On adding excess chlorine water, the colour will disappear because free iodine is oxidized to iodic acid:

$$\begin{array}{r|l} 1 & I_2 + 6H_2O - 10e = 2HIO_3 + 10H^+ \\ 5 & Cl_2 + 2e = 2Cl^- \end{array}$$
$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10Cl^- + 10H^+$$

2. Potassium nitrite or sodium nitrite in acidic solutions oxidizes iodide ions to elementary iodine (in contrast to chloride and bromide ions):

$$2KI + 2HNO_2 + H_2SO_4 = I_2 + 2NO + K_2SO_4 + 2H_2O$$
$$2I^- + 2NO_2^- + 4H^+ = I_2 + 2NO + 2H_2O$$

Procedure. To 2 or 3 drops of the solution under test add 1 or 2 drops of $2N$ H_2SO_4 solution, 2 or 3 drops of starch solution, and 1 or 2 drops of KNO_2 or $NaNO_2$. In the presence of iodide ions, the solution will turn blue.

97. Tests for Sulphide Ion, S^{2-}

The S^{2-} ion is the anion of hydrosulphuric acid, an aqueous solution of hydrogen sulphide. Hydrosulphuric acid is a weak acid and a strong oxidizing agent. It forms neutral salts called sulphides and acid salts called hydrosulphides.

The sulphides of alkali and alkaline earth metals and ammonium sulphide are soluble in water; the other sulphides are insoluble in water. The S^{2-} ion is colourless.

1. Hydrochloric acid and other dilute acids on reacting with soluble sulphides and certain insoluble sulphides liberate hydrogen sulphide:

$$Na_2S + 2HCl = H_2S \uparrow + 2NaCl$$

$$S^{2-} + 2H^+ = H_2S \uparrow$$

which can be detected by its odour and if a piece of filter paper moistened with lead acetate solution turns black or a piece of filter paper moistened with an antimony salt solution turns orange.

Procedure. Moisten a strip of filter paper with lead acetate solution or a solution of antimonic or antimonous chloride. To 2 or 3 drops of the solution under test add 3-4 ml of 2*N* HCl solution. Cover the test tube with the strip of filter paper and heat gently. In the presence of sulphide ion, the paper will turn black if it is moistened with lead acetate solution or will turn orange if it is moistened with an antimony salt solution.

2. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, in the presence of sulphide ions in an alkaline solution produces a red-violet coloration due to the formation of the complex ion $[Fe(CN)_5NOS]^{4-}$. The presence of SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-} ions do not interfere with this test.

Procedure. Place a drop of the solution under test on a spot plate, add a drop of 2*N* alkali hydroxide solution and a drop of 1 per cent sodium nitroprusside solution. In the presence of sulphide ion the mixture will become red-violet in colour.

98. Analysis of Mixture of Group I Anions

1. Test for presence of Group I anions. To 3-5 drops of the solution under test add 2-3 ml of 2*N* HNO_3 solution and 0.1*N* $AgNO_3$ solution a drop at a time. If no precipitate is formed, Group I anions are absent; if a precipitate is formed, Group I anions are present. The precipitate will be black in the presence of S^{2-} ions, yellow in the presence of I^- ions,

light yellow in the presence of Br^- ions, white in the presence of Cl^- ions.

Since the solubility of AgI is considerably lower than that of AgBr and AgCl, on adding $AgNO_3$ solution gradually to a solution containing Cl^-, Br^-, and I^- ions, first a yellow precipitate of AgI will be formed and then a light yellow precipitate of AgBr and a white precipitate of AgCl.

2. Preliminary tests. (a) Apply to starch-iodide paper a drop of $2N$ HCl solution, a drop of KNO_2 solution, and a drop of the solution under test. The presence of iodide ions, I^-, is indicated if the paper turns blue. (b) Moisten a piece of filter paper with an alkaline solution of lead acetate [1] and apply a drop of the solution under test to it. Blackening of the paper shows that sulphide ions, S^{2-}, are present.

3. Test for sulphide ion (see Sec. 97).

4. Test for iodide ion (see Sec. 96).

5. Test for bromide ion. To 5-8 drops of the solution under test add 3 ml of $2N$ H_2SO_4 solution, 2 ml of benzene (or any other organic solvent) and a few drops of chlorine water. Shake the mixture vigorously. In the presence of I^- ions the benzene layer will turn a red-violet colour even when bromide ions are also present. If there are no I^- ions in the solution under test the benzene layer will turn a straw-yellow colour in the presence of bromide ions. If there are neither I^- nor Br^- ions in the solution under test the benzene layer will be colourless.

If on adding chlorine water to the solution under test the benzene layer turns red-violet, in order to detect Br^- ions, continue to add chlorine water gradually, shaking the mixture vigorously, until the benzene layer turns yellow (in the presence of Br^- ions) or becomes colourless (in the absence of Br^- ions).

The presence of SO_3^{2-} and $S_2O_3^{2-}$ ions interferes with this test because they are stronger reducing agents than I^- and Br^- and they are oxidized by chlorine water sooner than I^- and Br^- ions. Therefore, a violet or yellow colour due to

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[1] Add excess NaOH to $Pb(CH_3COO)_2$ until the precipitate that appears at first is dissolved. This solution is used to moisten a piece of filter paper.

the presence of iodide or bromide ions will not appear even when a large quantity of chlorine water is added. If SO_3^{2-} or $S_2O_3^{2-}$ ions are present, it is necessary to first add 1 ml of $2N$ H_2SO_4 solution and a few drops of H_2O_2.

6. Test for chloride ions. If no Br^-, I^-, or S^{2-} ions are present in the solution, Cl^- ions are detected in the following way: to 3-5 drops of the solution under test add 3-5 drops of $AgNO_3$ solution and 1 ml of $6N$ HNO_3 solution. Heat the mixture to boiling and centrifuge. Wash the precipitate 2 or 3 times with hot water and treat with NH_4OH. Add to the clear ammoniacal solution $2N$ HNO_3 until the solution is acidic to litmus. The formation of a white precipitate indicates the presence of Cl^- ions.

In the presence of Br^- and I^- ions, Cl^- ions are detected in the following way. To 1 ml of the solution under test add 2 ml of $6N$ HNO_3 solution and 1 ml of $AgNO_3$ solution. Shake the mixture, place the test tube in a boiling water bath and, after several minutes have elapsed, centrifuge. Then check for completeness of precipitation of the silver halides by adding 1 or 2 drops of $0.1N$ $AgNO_3$ solution to the supernatant. If precipitation is complete, no suspended matter whatever should appear.

After making sure that precipitation of the silver halides is complete, separate the precipitate from the supernatant. Discard the supernatant and wash the precipitate with hot water until the wash water is free from Ag^+ ions (no precipitate is formed in the wash water on adding HCl). Transfer the precipitate to a test tube. Add 2-3 ml of a saturated solution of $(NH_4)_2CO_3$ and 1 ml of aqueous ammonia solution (1:1). In this mixture AgCl is dissolved with the formation of the complex salts $[Ag(NH_3)_2]_2CO_3$ and $[Ag(NH_3)_2]Cl$, while AgI and AgBr are not dissolved in it. Shake the mixture vigorously for 1 minute and centrifuge. Divide the supernatant into two portions. To one of them add $2N$ HNO_3 until the solution is acidic to litmus; the appearance of white suspended matter shows that Cl^- ions are present. To the other portion of the supernatant add 3-5 drops of KI. The appearance of a yellow precipitate or suspended matter shows that Cl^- ions are present because AgI is considerably less soluble than AgCl and the I^- ion precipitates the Ag^+ ion from the complex salt $[Ag(NH_3)_2]Cl$.

CHAPTER XX

Group II Anions

(CO_3^{2-}, BO_3^{3-}, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, AsO_3^{3-}, AsO_4^{3-}, CrO_4^{2-}, SiO_3^{2-})

Group II anions form precipitates with $BaCl_2$ and $AgNO_3$ that dissolve in HNO_3. An exception is the SO_4^{2-} ion which does not form a precipitate in dilute $AgNO_3$ solution and with $BaCl_2$ forms a precipitate that is insoluble in HNO_3. Group II anions are the acid radicals of carbonic, boric, sulphuric, sulphurous, thiosulphuric, phosphoric, arsenic [1], arsenous, chromic, and silicic acids.

The SO_3^{2-}, $S_2O_3^{2-}$, and AsO_3^{3-} ions are reducing agents; SO_4^{2-} in concentrated H_2SO_4 and the CrO_4^{2-}, $Cr_2O_7^{2-}$, and AsO_4^{3-} ions are oxidizing agents.

Although the SO_3^{2-} ion is a reducing agent, it also exhibits weak oxidizing properties.

99. Reactions of Group II Anions

When studying the reactions for identifying Group II anions, from 3 to 5 drops of their solutions should be taken for each test.

1. Barium chloride reacts with salts of all the Group II anions to form precipitates of a white colour, with the exception of $BaCrO_4$ which is yellow. All the precipitates, except $BaSO_4$, are soluble in nitric acid.

Procedure. To solutions of Na_2CO_3, $Na_2B_4O_7$, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, Na_2HPO_4, and Na_2SiO_3 contained in separate test tubes add 2 or 3 drops of barium chloride solution. A white precipitate will appear in all the test tubes. Barium metaborate, $Ba(BO_2)_2$, is precipitated only from concentrated solutions. Barium thiosulphate, BaS_2O_3, is precipitated only on adding excess $BaCl_2$. Treat each precipitate with nitric acid. All the precipitates are dissolved except $BaSO_4$.

2. Silver nitrate forms precipitates with salts of all the Group II anions. Silver sulphate is precipitated only when concentrated solutions of $AgNO_3$ react with soluble sulphates. The silver salts formed with all the Group II acids are

[1] The analytical properties of AsO_3^{3-}, AsO_4^{3-}, and CrO_4^{2-} anions have already been discussed when studying the cations.

soluble in HNO_3 except $Ag_2S_2O_3$ which is converted to Ag_2S (see Sec. 104, *P* 1).

The precipitates of Ag_2CO_3, $AgBO_2$, Ag_2SO_4, Ag_2SO_3 are white; those of Ag_3PO_4, Ag_3AsO_3, Ag_2SiO_3 are light-yellow; Ag_3AsO_4 is reddish-brown; Ag_2CrO_4 is brick-red. Silver thiosulphate, $Ag_2S_2O_3$, is a white compound that rapidly turns yellow, then brown, and finally black.

Procedure. To separate test tubes containing 2 or 3 drops of the Group II sodium salts add 2 or 3 drops of $AgNO_3$. Make a note of the colour of each precipitate formed. Treat them with 2*N* HNO_3 solution. All the precipitates are dissolved in HNO_3 except silver thiosulphate.

3. Mineral acids decompose the carbonates, sulphates, and thiosulphates, evolving CO_2, SO_2, and S, respectively. Carbonates are decomposed even by acetic acid.

Procedure. To 2 or 3 drops of solutions of a carbonate, sulphate, and thiosulphate contained in separate test tubes add 2 or 3 drops of 2*N* HCl solution. A gas will be evolved in all the test tubes.

100. Test for Carbonate Ion, CO_3^{2-}

The CO_3^{2-} ion is the anion of carbonic acid, H_2CO_3, which exists only in aqueous solutions. Carbonic acid is a weak acid. It forms neutral salts called carbonates and acid salts called hydrocarbonates (bicarbonates). The only carbonates that are soluble in water are those of the alkali metals and ammonium. Carbonates that are insoluble in water dissolve in acetic acid and mineral acids.

Dilute acids, including acetic acid, decompose all the carbonates, evolving carbon dioxide, CO_2, which can be detected by passing it into lime water (calcium hydroxide solution) or baryta water (barium hydroxide solution); a milkiness appears:

$$Na_2CO_3 + 2HCl = H_2CO_3 + 2NaCl$$

$$CO_3^{2-} + 2H^+ = H_2CO_3 \rightarrow H_2O + CO_2\uparrow$$

$$CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O$$

Procedure. Assemble the apparatus shown in Fig. 12. Fill the pipette capillary with lime water or baryta water. Place in the test tube 5-8 drops of the solution under test

and 5-8 drops of 2*N* HCl solution. Close the test tube loosely with a stopper carrying the pipette as quickly as possible and insert the test tube in a boiling water bath. In the presence of CO_3^{2-} ions the solution in the capillary will become milky. If the carbon dioxide acts on the mixture in the capillary for a long time, the milkiness will disappear because of the formation of the water-soluble calcium (or barium) bicarbonate:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

Sulphites and thiosulphates, on reacting with mineral acids, evolve sulphur dioxide which, like carbon dioxide, produces a milky solution with lime water or baryta water due to the precipitation of the insoluble salts, $BaSO_3$ and BaS_2O_3. Therefore, to detect CO_3^{2-} in the presence of SO_3^{2-} and $S_2O_3^{2-}$ ions it is necessary to previously add 1 or 2 drops of hydrogen peroxide to the solution and to boil it for 2-3 minutes in order to oxidize the SO_3^{2-} and $S_2O_3^{2-}$ ions to SO_4^{2-}.

Fig. 12. Apparatus for detecting evolution of gas

101. Test for Borate Ion, BO_3^{3-}

The $B_4O_7^{2-}$ and BO_2^- ions are the anions of pyroboric and metaboric acids, respectively. Three boric acids are known: H_3BO_3, boric (orthoboric) acid; $H_2B_4O_7$, tetraboric (pyroboric) acid; and HBO_2, metaboric acid. These are all weak acids that are even weaker than carbonic and hydrosulphuric acids.

The boric acids form salts called borates, metaborates, and pyroborates.

Boric acid, H_3BO_3, is a solid crystalline substance. No salts of this acid are known. Borates are derivatives of metaboric and pyroboric acids, the most important one being sodium tetraborate, $Na_2B_4O_7$, called borax. Since borax is a salt of a very weak acid, its aqueous solution is hydrolyzed and has a strongly alkaline reaction (pH $\approx$ 11):

$$Na_2B_4O_7 + 7H_2O \rightleftarrows 4H_3BO_3 + 2NaOH$$

$$B_4O_7^{2-} + 7H_2O \rightleftarrows 4H_3BO_3 + 2OH^-$$

The only borates that are soluble in water are those of the alkali metals.

Alcohol and concentrated sulphuric acid, on heating, react with dry borates to form methyl or ethyl borate which imparts a characteristic green colour to a gas flame or burning alcohol.

When methyl alcohol is used for this reaction, the volatile methyl borate, $B(OCH_3)_3$, is formed:

$$H_3BO_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O$$

The reaction with ethyl alcohol proceeds in a similar way. The presence of barium salts, copper chloride, and copper bromide interferes with the detection of borate ions by this reaction because they also give a green coloration to the flame.

Procedure (carry out the test in a fume cupboard!). Evaporate 0.5-1 ml of the solution under test to dryness in an evaporating dish or crucible. Allow the dry residue to cool, moisten it with 2-3 ml of methyl or ethyl alcohol, and add 2 or 3 drops of concentrated H_2SO_4. Stir the mixture thoroughly with a glass rod and ignite. In the presence of borate ions the flame will have a green colour.

102. Test for Sulphate Ion, SO_4^{2-}

The SO_4^{2-} ion is the anion of sulphuric acid, H_2SO_4. Sulphuric acid is a strong acid. It forms salts called sulphates. All sulphates are readily soluble in water except barium, strontium, calcium, lead, and silver sulphates.

Barium chloride reacts with sulphate solutions to form $BaSO_4$, a white precipitate that is insoluble in acids.

Procedure. Add to 3-5 drops of the solution under test 1 ml of $2N$ HNO_3 solution and 2 or 3 drops of $2N$ $BaCl_2$ solution. In the presence of sulphate ions a white precipitate is formed which is not dissolved on adding a new portion of HNO_3.

103. Tests for Sulphite Ion, SO_3^{2-}

The SO_3^{2-} ion is the anion of sulphurous acid, H_2SO_3, which exists only in aqueous solutions. Sulphurous acid, like carbonic acid, is unstable and decomposes to form SO_2 and H_2O. It is an acid of medium strength that forms salts

called sulphites. The only sulphites that are soluble in water are those of the alkali metals and ammonium. Sulphurous acid and sulphites are strong reducing agents and weak oxidizing agents.

1. Dilute mineral acids from solutions of all the metallic sulphides liberate sulphur dioxide which decolourizes potassium permanganate and iodine solutions:

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2\uparrow + H_2O$$
$$SO_3^{2-} + 2H^+ = H_2SO_3 \rightarrow H_2O + SO_2\uparrow$$
$$5SO_2 + 2KMnO_4 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$
$$5SO_2 + 2MnO_4^- + 2H_2O = 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

Procedure. Place 5-8 drops of the solution under test and 5 or 6 drops of 2*N* HCl in the test tube of the apparatus (see Fig. 12) in which the pipette capillary has been filled with dilute $KMnO_4$ (purple solution). Heat the test tube gently in a water bath. In the presence of SO_3^{2-} ions the liquid in the capillary is decolourized.

2. Zinc in the presence of hydrochloric acid reduces sulphites to sulphides. The S^{2-} ions formed can be detected by the reaction with Pb^{2+}. This method cannot be used to detect sulphites if S^{2-} and $S_2O_3^{2-}$ ions are present in the solution under test.

Procedure. Place 5-8 drops of the solution under test in the test tube of the tester (see Fig. 12) in which the pipette capillary has been filled with $Pb(CH_3COO)_2$ solution. In the test tube place a piece of zinc and add 5-8 drops of 2*N* HCl solution. Heat the test tube in a water bath. In the presence of sulphite ions the liquid in the capillary will turn black due to the formation of a precipitate of PbS.

3. Iodine or bromine in aqueous solution (bromine or iodine water) **and potassium permanganate in an acidic solution** oxidize the SO_3^{2-} ion to SO_4^{2-} and are themselves decolourized (reduced to I^-, Br^-, or Mn^{2+}) for example:

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$$
$$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2I^- + 2H^+$$
$$5Na_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 5Na_2SO_4 + 2MnSO_4 + K_2SO_4 + 3H_2O$$
$$5 \mid SO_3^{2-} + H_2O - 2e = SO_4^{2-} + 2H^+$$
$$2 \mid MnO_4^- + 8H^+ + 5e \quad Mn^{2+} + 4H_2O$$
$$5SO_3^{2-} + 2MnO_4^- + 6H^+ = 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$$

The presence of reducing agents in the solution interferes with the detection of sulphite ions.

Procedure. To 5 or 6 drops of the solution under test add 5-8 drops of $2N$ H_2SO_4 solution and iodine or bromine water or dilute $KMnO_4$ solution drop by drop. In the presence of SO_3^{2-} ion these reagents will be decolourized.

104. Tests for Thiosulphate Ion, $S_2O_3^{2-}$

The $S_2O_3^{2-}$ ion is the anion of thiosulphuric acid, $H_2S_2O_3$, which is unstable even in aqueous solutions [1] and decomposes to form sulphurous acid and elementary sulphur:

$$H_2S_2O_3 \rightleftarrows H_2SO_3 + S$$

The salts of thiosulphuric acid are called thiosulphates. The thiosulphates of Groups I, II, and III cations are soluble in water; those of Group IV are insoluble except cadmium thiosulphate (which is readily soluble) and barium thiosulphate (which is slightly soluble). Thiosulphates are strong reducing agents and weak oxidizing agents.

1. Silver nitrate forms with thiosulphates a white precipitate of silver thiosulphate, $Ag_2S_2O_3$, that rapidly changes colour: first it turns yellow, then brown, and finally black as the white precipitate of silver thiosulphate is converted to the black silver sulphide:

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

2. Dilute mineral acids decompose thiosulphates, producing sulphur and liberating SO_2:

$$Na_2S_2O_3 + H_2SO_4 = S\downarrow + SO_2\uparrow + Na_2SO_4 + H_2O$$

$$S_2O_3^{2-} + 2H^+ = S\downarrow + SO_2\uparrow + H_2O$$

Procedure. To 3-5 drops of the solution under test add 3-5 drops of $2N$ H_2SO_4. In the presence of $S_2O_3^{2-}$ ions a white-yellow precipitate of sulphur will be formed.

3. Iodine water or protassium permanganate solution when added to thiosulphate solutions is decolourized; the $S_2O_3^{2-}$ ion is oxidized by iodine to the tetrathiosulphate,

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[1] Thiosulphuric acid has not been isolated in the free state; it decomposes even in dilute aqueous solutions.

$S_4O_6^{2-}$, and by potassium permanganate to the sulphate ion, SO_4^{2-}:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

$$\begin{array}{r|l} 1 & 2S_2O_3^{2-} - 2e = S_4O_6^{2-} \\ 1 & I_2 + 2e = 2I^- \end{array}$$

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

$$5Na_2S_2O_3 + 8KMnO_4 + 7H_2SO_4 = 5Na_2SO_4 +$$

$$+ 8MnSO_4 + 4K_2SO_4 + 7H_2O$$

$$5S_2O_3^{2-} + 8MnO_4^- + 14H^+ = 10SO_4^{2-} + 8Mn^{2+} + 7H_2O$$

$$\begin{array}{r|l} 5 & S_2O_3^{2-} + 5H_2O - 8e = 2SO_4^{2-} + 10H^+ \\ 8 & MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \end{array}$$

Procedure. To 5 or 6 drops of the solution under test add 2 or 3 drops of 2*N* H_2SO_4 and iodine water or dilute $KMnO_4$ solution. In the presence of thiosulphate ion both of the reagents are decolourized. This reaction cannot be used to detect $S_2O_3^{2-}$ ions if the solution contains reducing agents.

105. Tests for Phosphate Ion, PO_4^{3-}

The PO_4^{3-} ion is the anion of orthophosphoric acid, H_3PO_4, which is a solid crystalline substance that is deliquescent in the air. Orthophosphoric acid (or simply phosphoric acid) in aqueous solutions dissociates in 3 stages: the first hydrogen ion dissociated acts like an acid of medium strength; the second and third hydrogen ions, like a weak acid. The only water-soluble phosphates are those of the alkali metals and ammonium as well as dihydrogen phosphates of the alkaline earth metals, for example, $Ca(H_2PO_4)_2$.

1. Magnesia mixture (an aqueous solution of $MgCl_2$, NH_4Cl, and NH_4OH) precipitates PO_4^{3-} ions from phosphate solutions in the form of a white crystalline precipitate of $MgNH_4PO_4$ that is readily soluble in acids and insoluble in ammonia solution.

Procedure. To 5 or 6 drops of the solution under test add 1 ml of 2*N* HCl solution and 3-5 drops of magnesia mixture. No precipitate should appear. If, however, a precipitate

does appear, add $2N$ HCl solution drop by drop until the precipitate is dissolved. To the clear solution add one drop of phenolphthalein and $6N$ ammonia solution a drop at a time, shaking the test tube after adding each drop, until the solution acquires a persistent red coloration. A white crystalline precipitate will appear in the presence of phosphate ion.

2. Ammonium molybdate in nitric acid solutions of phosphates forms, on heating, a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PMo_{12}O_{40}$:

$$3NH_4^+ + PO_4^{3-} + 12MoO_4^{2-} + 24H^+ = (NH_4)_3PMo_{12}O_{40} + 12H_2O$$

The precipitate readily dissolves in the alkali hydroxides and ammonia solution and does not dissolve in nitric acid. The presence of AsO_4^{3-} ion interferes with the detection of PO_4^{3-} by this reaction because AsO_4^{3-} reacts in the same way.

Procedure. Add to 5-8 drops of the solution under test 1 ml of $2N$ HNO_3 solution and 1-2 ml of a nitric acid solution of ammonium molybdate, $(NH_4)_2MoO_4$. Boil the solution. In the presence of phosphate ion a yellow precipitate of $(NH_4)_3PMo_{12}O_{40}$ will appear.

106. Tests for Silicate Ion, SiO_3^{2-}

The SiO_3^{2-} ion is the anion of silicic (metasilicic) acid, H_2SiO_3. Silicic acid is a weak acid that is practically insoluble in water. Dried silicic acid is known as silica gel.

The only water-soluble silicates are those of sodium and potassium, Na_2SiO_3 and K_2SiO_3, called soluble glass.

1. Dilute mineral acids precipitate silicic acid from solutions of silicates of the alkali metals.

Procedure. Add to 1-2 ml of the solution under test one drop of phenolphthalein (the solution turns pink) and $2N$ solution of a mineral acid a drop at a time, shaking thoroughly after adding each drop. Continue to add the acid until the pink colour of the solution disappears. A gelatinous precipitate of metasilicic acid will appear in the presence of silicate ion.

2. Ammonium chloride precipitates silicic acid when heated with solutions of silicates.

Procedure. To 1-2 ml of the solution under test add 1-2 ml of 2*N* NH_4Cl. Heat the mixture to boiling. In the presence of silicate ion metasilicic acid will be precipitated.

107. Analysis of Mixture of Group II Anions

1. Test for Group II anions and sulphate ion, SO_4^{2-}. To 3-5 drops of the solution under test (pH $\approx$ 7-9)[1] add 6-8 drops of 2*N* $BaCl_2$ solution. The appearance of a precipitate shows that Group II anions are present[2]. Centrifuge the mixture, treat the precipitate with 2*N* HNO_3 solution. If the precipitate is dissolved, the absence of SO_4^{2-} ions in the solution under test is indicated. The presence of $BaSO_4$, i.e., of sulphate ions in the original solution, is indicated if the precipitate is not dissolved.

2. Test for thiosulphate ion, $S_2O_3^{2-}$, (see Sec. 104*P* 1).

3. Test for sulphite ion, SO_3^{2-}, in the absence of thiosulphate ion, $S_2O_3^{2-}$. To 5-8 drops of the solution under test add 1-2 ml of 2*N* HCl solution and 8-10 drops of 2*N* $BaCl_2$ solution. If a precipitate appears, centrifuge and separate the precipitate from the solution. To the clear solution add 5-8 drops of H_2O_2. The appearance of a white precipitate shows that SO_3^{2-} ions are present.

4. Test for sulphite ion, SO_3^{2-}, in the presence of thiosulphate ion, $S_2O_3^{2-}$. To 5-8 drops of the solution under test add 5 or 6 drops of 2*N* $Sr(NO_3)_2$ solution. Centrifuge the mixture, wash the precipitate with hot water, and treat it with 1 or 2 drops of 0.1*N* iodine water. The disappearance of the coloration due to iodine confirms the presence of SO_3^{2-} ions.

5. Test for carbonate ion, CO_3^{2-} (see Sec. 100).

6. Test for phosphate ion, PO_4^{3-} (see Sec. 105, *P* 2).

7. Test for chromate ion, CrO_4^{2-} (see Sec. 56, *P* 4).

8. Test for borate ion, BO_3^{3-} (see Sec. 101).

9. Test for silicate ion, SiO_3^{2-} (see Sec. 106, *P* 2).

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[1] Acidic solutions are neutralized with $Ba(OH)_2$.

[2] $S_2O_3^{2-}$ and BO_3^{3-} anions may be present even if no precipitate appears, because these anions are precipitated by Ba^{2+} ions only from concentrated solutions.

CHAPTER XXI

Group III Anions

(NO_3^-, NO_2^-)

Group III anions do not form precipitates with $AgNO_3$ or with $BaCl_2$. In this textbook the following Group III anions are discussed: the nitrate ion, NO_3^-, and the nitrite ion, NO_2^-.

108. Tests for Nitrate Ion, NO_3^-, and Nitrite Ion, NO_2^-

The nitrate ion, NO_3^-, is the anion of nitric acid; the nitrite ion, NO_2^-, of nitrous acid. Nitric acid is one of the strongest mineral acids; nitrous acid is a weak acid.

Nitric acid, especially concentrated nitric acid, is a strong oxidizing agent. Nitrous acid can be an oxidizing and a reducing agent. Thus, nitrous acid oxidizes the iodide ion:

$$2HNO_2 + 2KI + 2HCl = 2NO\uparrow + I_2 + 2KCl + 2H_2O$$

$$2NO_2^- + 2I^- + 4H^+ = 2NO\uparrow + I_2 + 2H_2O$$

and reduces strong oxidizing agents, for example, potassium permanganate:

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

$$5HNO_2 + 2MnO_4^- + H^+ = 5NO_3^- + 2Mn^{2+} + 3H_2O$$

The salts of nitric acid are called nitrates; those of nitrous acid are called nitrites. All the nitrates and nitrites are readily soluble in water except the basic nitrates (subnitrates) of bismuth, antimony, and mercury; silver nitrite, $AgNO_2$, is sparingly soluble in water.

TEST FOR NITRATE ION, NO_3^-

Diphenylamine with NO_3^- ions produces an intense blue coloration. This is a very sensitive test but it is not specific since the same colour is produced by other oxidizing agents, such as nitrites, chromates, and permanganates.

Procedure. Place in a small evaporating dish or on a spot plate one crystal of diphenylamine and 1 ml of concentra-

ted chemically pure H_2SO_4. Carefully add with the aid of a dropper pipette 1 or 2 drops of the solution under test. The presence of nitrates or other oxidizing agents will give the mixture an intense blue colour.

TESTS FOR NITRITE ION, NO_2^-

1. A mixture of sulphanilic acid and α-naphthylamine (Griess' reagent) imparts a cherry-red colour to the solution if traces of nitrite ions are present in it.

Procedure. Rinse a test tube with the solution under test. Place in it 3-5 ml of distilled water and 2 or 3 drops of sulphanilic acid solution and the same quantity of α-naphthylamine (Griess' reagent, see Appendix 3B). In the presence of small quantities of nitrite ions a cherry-red colour will appear.

2. Potassium iodide in slightly acidic solutions is oxidized by the nitrite ion to free iodine:

$$2NO_2^- + 2I^- + 4H^+ = I_2 + 2NO\uparrow + 2H_2O$$

The presence of NO_3^- ions does not interfere with this test, but that of oxidizing agents does.

Procedure. To a strip of filter paper apply a drop of starch solution, a drop of $2N$ CH_3COOH solution and a drop of $0.1N$ KI solution; no blue coloration should appear. The appearance of a blue ring or stain on the filter paper after adding a drop of the solution under test confirms the presence of nitrite ions.

109. Analysis of Mixture of Group III Anions

There is no group precipitant for Group III anions. They are detected by the method of separation or isolation.

1. Test for nitrite ions, NO_2^-, (see Sec. 108, *P* 1).

2. Test for nitrate ions, NO_3^-, in the absence of nitrite ions, NO_2^-, and other oxidizing agents (see Sec. 108).

3. Test for nitrate ions, NO_3^-, in the presence of nitrite ions, NO_2^-, but in the absence of other oxidizing agents. To 1 ml of water add 5 or 6 drops of the solution under test and gradually, in small portions, powdered amidosulphonic acid, shaking the test tube vigorously after adding each portion.

Continue to add the amidosulphonic acid until gas (N_2) is no longer liberated. After the nitrite has been completely converted to N_2, test for NO_3^- ions with diphenylamine (see Sec. 108).

Review Questions

1. What are the characteristic reactions for each group of anions?
2. What anions are oxidizing agents and what anions are reducing agents?
3. How is the presence of a reducing agent detected in the solution under test?
4. How is the presence of an oxidizing agent detected in the solution under test?
5. How is the Cl^- ion detected in the absence of Br^- and I^- ions and how is it detected if they are present?

CHAPTER XXII

Systematic Analysis of Mixture of Anions

110. Preliminary Tests

1. Determination of the pH-value in the solution under test. Apply 2 or 3 drops of the solution under test to a strip of indicator paper and determine approximately the pH-value of the solution by the resultant colour. If the acidity of the solution under test is high (the pH is equal to or less than 2) no volatile acids can be present in it.

2. Test for presence of ions of volatile acids. To 2-3 ml of the solution under test or to 0.25 g of the dry substance, taken in the form of a fine powder, add 2-3 ml of 2*N* HCl solution. Shake the mixture and heat it gently. If a gas is liberated, CO_3^{2-}, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and NO_2^- ions may possibly be present in the mixture. Note the colour and odour of the gases liberated: a brown gas (NO_2) indicates the presence of NO_2^- ions; an unpleasant odour resembling that of rotten eggs (H_2S) shows that S^{2-} ions are present; a characteristic pungent odour (SO_2) indicates the presence of SO_3^{2-} or $S_2O_3^{2-}$ ions in the mixture. The appearance of a precipitate or turbidity on adding HCl solution to a solution under test that does not contain the silver subgroup indi-

cates the presence of $S_2O_3^{2-}$ or SiO_3^{2-} ions (although the latter may fail to produce a precipitate).

3. Test for carbonate ion, CO_3^{2-} (see Sec. 100).

4. Test for presence of ions of heavy metals. To 5-8 drops of the solution under test add 0.5 ml of NH_4Cl solution and $2N$ NH_4OH solution until the solution is alkaline to litmus. Pass H_2S into the resulting mixture. The appearance of a coloured precipitate indicates the presence of heavy metals which are removed by precipitating them with a carbonate (usually Na_2CO_3) or by the chromatographic method (see Chapter LVI).

5. Separation of ions of heavy metals[1] (preparation of solution for analysis of anions). **Treatment with sodium carbonate to obtain the 'soda extract'.** To 3-5 ml of the solution under test or to 1-2 g of the dry substance add 3-5 ml of $3N$ Na_2CO_3 solution. Boil the mixture carefully for 3-5 minutes, stirring it with a glass rod and adding distilled water as the liquid evaporates. Filter or centrifuge the mixture. Reserve the precipitate for analysis of the anions that did not pass into solution. The supernatant (or filtrate) obtained, freed from cations of heavy metals, is used for testing for anions.

6. Test for presence of oxidizing agents. To 1 ml of the solution freed from cations of heavy metals, add $2N$ HCl until the solution is acidic to litmus then 0.5 ml of starch solution, and 0.5 ml of $2N$ KI solution. The presence of oxidizing agents (NO_2^-, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, and AsO_4^{3-}) and the absence of reducing agents is indicated if the solution turns blue [2].

7. Test for presence of reducing agents. To 1 ml of the solution freed from cations of heavy metals add $2N$ HCl until the solution is acidic to litmus and then $0.1N$ iodine water drop by drop. Note the change in colour of the solution after adding each drop. Decoloration of the iodine indicates the presence of reducing agents (S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, AsO_3^{3-}) and the absence of oxidizing agents.

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[1] If the substance under test contains only the alkali metals, the analysis of anions can be conducted on the original solution.

[2] First check the purity of the KI solution; it should not turn blue on adding starch solution and HCl to it.

8. **Test for presence of Group I anions.** To 1 ml of the solution freed from cations of heavy metals add 1 ml of $6N$ HNO_3 solution and 1 ml of $0.1N$ $AgNO_3$ solution. Precipitation of silver salts that are not dissolved on further addition of HNO_3 indicates the presence of Group I anions. The appearance of a white precipitate that gradually grows black shows that $S_2O_3^{2-}$ ions are present.

9. **Test for presence of Group II anions.** To 1 ml of the solution freed from cations of heavy metals add 1 ml of water and $2N$ CH_3COOH solution a drop at a time until the solution is acidic to litmus. Then add another 0.5 ml of $2N$ CH_3COOH solution. Boil the solution for 2-3 minutes to completely remove CO_2, cool, and add 0.5 ml of $2N$ $BaCl_2$ solution. The appearance of a precipitate indicates the presence of Group II anions.

111. Systematic Scheme of Analysis

In the systematic analysis of the anions it is not advisable to test for anions the absence of which has previously been definitely ascertained.

1. **Test for nitrite ion, NO_2^-,** (see Sec. 108, *P* 1).
2. **Test for nitrate ion, NO_3^-,** (see Sec. 108).
3. **Test for Group I anions** (see Sec. 98, *P* 1).
4. **Test for sulphate ion, SO_4^{2-}, and thiosulphate ion, $S_2O_3^{2-}$ in the absence of silicate ions, SiO_3^{2-}.** To 2 ml of the solution add $2N$ HCl to make the solution acidic and boil the mixture. The absence of any precipitate shows that $S_2O_3^{2-}$ ions are absent. After that add $2N$ $BaCl_2$ solution. The appearance of a precipitate that is insoluble in $6N$ HNO_3 indicates the presence of SO_4^{2-} ions.
5. **Test for sulphide ion, S^{2-},** (see Sec. 97).
6. **Test for sulphite ion, SO_3^{2-}.** To 1 ml of the solution under test add 1 ml of $Sr(NO_3)_2$ solution. $SrSO_4$ and $SrSO_3$ will be precipitated. Filter or centrifuge the mixture. Discard the solution; wash the precipitate with water and then wet it with 1 or 2 drops of $0.1N$ iodine water and 2 or 3 drops of $2N$ HCl solution. Disappearance of the characteristic colour of iodine indicates the presence of SO_3^{2-} ions.
7. **Test for phosphate ion, PO_4^{3-},** in the absence of arsenic. To 1 ml of the solution under test add $2N$ HNO_3 to obtain

an acidic solution and 1 ml of ammonium molybdate solution and boil for 1-2 minutes. The appearance of a yellow precipitate indicates the presence of PO_4^{3-} ions.

8. **Test for borate ion, BO_3^{3-},** by the dry method (see Sec. 101).

9. **Test for silicate ion, SiO_3^{2-},** (see Sec. 106, *P* 2).

ANALYSIS OF AN UNKNOWN SUBSTANCE

CHAPTER XXIII

Test Procedures

112. Analysis of an Unknown Solution

1. **Preliminary tests.** Note the colour and odour of the solution in your laboratory notebook.

The presence of Co^{2+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Fe^{2+} ions can often be determined approximately by the colour of the solution (see Sec. 62, preceding *P* 1, and Sec. 90, *P* 1).

The presence of volatile compounds, such as NH_3, HCl, HNO_3, CH_3COOH, H_2S can be detected by their odour.

2. **Flame tests.** Dip a clean calcined platinum wire into the solution under test, insert it in the nonluminous flame of a burner; note the colour of the flame and compare it with the following Table:

Flame Colorations Produced by Salts of Various Cations

Colour of flame	Cations
Violet or lilac, visible through cobalt glass or indigo prism	K^+
Orange-yellow, persisting during 20-30 seconds	Na^+
Crimson	Sr^{2+}
Brick-red	Ca^{2+}
Yellow-green	Ba^{2+}
Green-blue	Cu^{2+}

3. **Borax-bead tests.** Make a clear borax bead (a bead made of a phosphate of an alkali metal can also be used for this

test), dip it into the solution under test and heat it, first in the reducing flame and then in the oxidizing flame of a burner. The Table given below indicates the colours of the beads in the presence of different ions.

Colours of Borax Beads Produced by Salts of Various Cations

In reducing flame	In oxidizing flame	Cations
Pale emerald green	Pale green	Cr^{3+}
Blue	Blue	Co^{2+}
Red-brown	Green	Cu^{2+}
Colourless	Amethyst	Mn^{2+}
Grey	Red-brown	Ni^{2+}
Green	Pale yellow	Fe^{2+}, Fe^{3+}

4. The action of alkali hydroxides often makes it possible to detect the presence of certain ions by the colour of the precipitate formed and its solubility in excess alkali and in ammonia solution. To 3-5 drops of the solution under test add alkali hydroxide solution or ammonia solution drop by drop. Ascertain what ion is present by the colour of the precipitate formed and its solubility in excess alkali and ammonia solution (see the Table below).

5. Tests for presence of cation groups. To 1-2 ml of the solution under test add 1 ml of 2*N* HCl solution. The appearance of a white precipitate indicates the presence of cations of the silver subgroup. Centrifuge and separate the precipitate from the solution and pass hydrogen sulphide into the clear solution until precipitation is complete. The precipitation of sulphides indicates the presence of Group IV and Group V cations. Ascertain approximately what cations of these groups are present by the colour of the precipitate (see Sec. 90, *P* 4). After centrifuging, separate the precipitate from the clear solution, neutralize the solution with ammonia solution until is weakly alkaline and add to it $(NH_4)_2S$ solution. The formation of a precipitate of hydroxides or sulphides is indication of the presence of Group III cations. Ascertain approximately what Group III cations are present by the colour of the precipitate. Centrifuge and

Action of Alkalies on Solutions under Test

Colour of precipitate	Solubility of precipitate in excess alkali	Solubility of precipitate in ammonia solution	Cations
White	Soluble	Soluble	Zn^{2+}
White	Soluble	Insoluble	Pb^{2+}, Al^{3+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}
White	Insoluble	Soluble	Cd^{2+}
White	Insoluble	Insoluble	Mg^{2+}, Bi^{3+}
White; turns brown in the air	Insoluble	Insoluble	Mn^{2+}
Pale green; turns brown in the air	Insoluble	Insoluble	Fe^{2+}
Red-brown	Insoluble	Insoluble	Fe^{3+}
Pale green	Insoluble	Soluble; produces a blue solution	Ni^{2+}
Blue; turns black on heating	Insoluble	Soluble; produces a blue solution	Cu^{2+}
Blue; turns pink-red on heating	Insoluble	Soluble; produces a yellow solution	Co^{2+}
Grey-green	Dissolves in the cold; on heating, is precipitated once more	Practically insoluble	Cr^{3+}
Yellow	Insoluble	Insoluble	Hg^{2+}

Continued

Colour of precipitate	Solubility of precipitate in excess alkali	Solubility of precipitate in ammonia solution	Cations
Brown-yellow	Insoluble	Soluble	Ag^+
Black	Insoluble	Insoluble	Hg^+ or Hg_2^{2+}
No precipitate appears	—	—	Cations of alkali and alkaline earth metals, ammonium, and arsenic

separate the precipitate from the solution after making sure that precipitation of Group III cations is complete. Acidify the clear solution with hydrochloric acid until the solution is acidic. Boil the solution to remove H_2S. Evaporate the remaining solution to dryness, ignite the residue to remove ammonium salts (until white fumes are no longer evolved). To the dry residue add 1-2 ml of water, 1 ml of NH_4Cl solution, and $2N$ NH_4OH solution until the reaction is alkaline. Heat the mixture to boiling and add to it $2N$ $(NH_4)_2CO_3$ solution. The precipitation of carbonates indicates the presence of Group II cations.

If the group analysis of the cations has shown that only one group is present, separate the cations of this group with the aid of the group reagent. Centrifuge and test the precipitate for cations of the given group. If the presence of several groups has been detected, analysis is conducted in accordance with the systematic scheme of analysis of mixtures containing salts of cations of all five groups (see Sec. 91). If the substance under test consists of a single salt, ascertain to which group the salt under test belongs and, in separate portions of the solution, conduct the identification tests for cations of the given group.

6. **Tests for oxidizing and reducing agents** (see Sec. 110, *P* 6 and *P* 7).

7. **Test for volatile acids** (see Sec. 110, *P* 2).

8. Analysis of the anions. If in addition to cations of the alkali and alkaline earth metals other cations have been found in the substance under test, a 'soda extract' should be prepared for analysis of the anions (see Sec. 110, *P* 5).

To 3-5 ml of the sample under test or the soda extract add 1 ml of 6*N* HNO_3 solution and 0.5 ml of 0.1*N* $AgNO_3$ solution. If a precipitate is formed that dissolves in 6*N* HNO_3, there are no Group I anions present in the solution; the formation of a precipitate that does not dissolve in HNO_3 shows that Group I anions are present.

To another portion of the solution under test (in the absence of heavy metals) add $BaCl_2$ solution. The appearance of a precipitate indicates the presence of Group II anions. Ascertain whether the precipitate formed dissolves in 6*N* HNO_3; if it does not dissolve, the presence of sulphate ions is indicated. If the solution under test contains heavy metals, the $BaCl_2$ solution should be added to 1 ml of the soda extract previously acidified with acetic acid (see Sec. 110, *P* 9).

Determine what anion groups the solution under test contains and carry out identification tests (see Sec. 111).

113. Analysis of an Unknown Solid (Nonmetal)

The solid under test is first subjected to preliminary analysis: (1) examine the substance under a magnifying glass or with the naked eye; (2) pulverize it, if necessary; (3) make flame tests; (4) dissolve it.

1. Estimation of homogeneity and crystalline character. Spread a portion of the sample under test in a thin even layer on a sheet of white paper and examine it with the naked eye in the presence of sufficient light or through a magnifying glass. Ascertain whether the sample consists of one, two, or more substances. Note the form and colour of individual particles in the sample.

2. Pulverization. A well-ground substance is more easily subjected to the action of reagents and solvents. Therefore, the substance under test should be ground to a powder. If the substance is relatively soft and brittle, it is ground in a porcelain or glass mortar. Very hard minerals, rocks, and slags are first broken into small pieces in a metal mortar and then ground to a fine powder in an agate mortar.

3. Flame tests. Wet a small quantity of the solid sample under test with a few drops of concentrated HCl solution. Touch a calcined platinum or nichrome wire to the solid material and place it in the nonluminous flame of a burner; make a note of the colour of the flame (see Sec. 112, *P* 2).

4. Dissolving of sample. In each of six test tubes place approximately 0.01-0.03 g of the finely ground sample. To the first test tube add 1 ml of water; to the second one, 1 ml of 2*N* HCl solution; to the third one, 1 ml of concentrated HCl solution; to the fourth one, 1 ml of 2*N* HNO_3 solution; to the fifth one, 0.5 ml of concentrated HNO_3; to the sixth one, 1 ml of 6*N* NaOH or KOH solution.

Heat each test tube in a water bath for 3-5 minutes, shaking the contents from time to time. Note in which test tube the sample is completely dissolved.

Certain substances do not dissolve in acids or in alkalies. Such substances are most of the silicates and sulphides of the alkaline earth metals. To convert them to the soluble form, fuse the sample with a mixture of Na_2CO_3 and K_2CO_3 or boil with Na_2CO_3 (see Sec. 38, *P* 7).

After selecting the appropriate solvent, treat 0.5 g of the sample under test with it and analyze the resulting solution as described in Sec. 112. If the substance is dissolved in nitric acid or in a mixture of nitric acid and hydrochloric acid, the solution obtained must be evaporated to dryness under a draft hood to remove HNO_3 which might interfere with further analysis. Dissolve the dry residue in water and analyze as described in Sec. 112.

If on dissolving the substance in acids, gases are liberated (CO_2, SO_2, H_2S, NO), make a note of their colour and odour. This is important in testing for the anions.

114. Analysis of a Metal or Alloy

Ferrous and non-ferrous metals[1] and their simplest alloys[2] can be analyzed by following the procedure described below.

[1] Ferrous alloys are iron-base alloys that may contain additions of Mn, Ni, Cr, V, Co, Mo, Cu, and C, P, Si. Non-ferrous alloys are copper-base alloys that may contain additions of Sn, Cd, Sb, Zn, Pb, Al, Mn, Bi, Fe, Ni, and P.

[2] The analysis of alloys containing rare and noble metals is not described in this textbook.

The analysis of a metal or alloy is carried out in the following order:

1. Dissolving of the sample and separation of antimony and tin ions. Place in a 150-200 ml beaker 0.3-0.5 g of the sample under test (fine filings or powder). Add 10 ml of HNO_3 (sp gr 1.2, i.e., a mixture of 1 volume of concentrated acid and 1 volume of water). Cover the beaker with a watch glass. Heat the mixture under a draft hood, using a small burner flame. Continue dissolving until the black metallic particles at the bottom of the beaker disappear. Continue to heat until brown fumes of oxides of nitrogen are no longer evolved. If antimony and tin ions are absent, the substance will be completely dissolved; the formation of a white precipitate indicates the presence of tin and antimony ions.

Wash the watch glass (on which there may be drops of the solution) with a jet of hot distilled water, holding it above the beaker. Transfer all of the mixture obtained to an evaporating dish and evaporate to dryness in a water bath. Transfer the dry residue to a beaker and add 1 ml of $2N$ HNO_3 solution and 5-10 ml of water. Stir the mixture thoroughly with a glass rod. If the alloy has dissolved completely, analyze the solution as described in *P* 3 et seq.; if any residue remains, centrifuge the mixture.

Precipitate 1: metastannic acid and metaantimonic acid; analyze as described in *P* 2.

Supernatant 1: all the metallic nitrates and PO_4^{3-} ions; analyze as described in *P* 3 et seq.

2. Test for antimony and tin. To precipitate 1 add 1-2 ml of hot $2N$ HNO_3 solution in order to convert antimony and tin to $HSbO_3$ and H_2SnO_3. Stir the mixture thoroughly and centrifuge. Add the solution obtained to supernatant 1. Wash the precipitate once more with $2N$ HNO_3 solution and 2 or 3 times with hot water. Transfer to an evaporating dish, add 2-3 ml of $2N$ KOH solution and concentrated K_2S solution. Heat the mixture in a water bath for 5-10 minutes, with stirring and centrifuge. Discard the precipitated sulphur and to the solution containing the thiosalts add 2-3 ml of water and concentrated HCl solution a drop at a time until the solution is acidic and heat to boiling; then centrifuge the mixture. Discard the solution containing salts of the alkali metals and wash the precipitate of Sb_2S_5 and

SnS_2 with hot water, dissolve it in concentrated hydrochloric acid and test the solution for antimony and tin ions (see Sec. 89, *P* 6 and *P* 7).

3. Separation of lead ions. Transfer supernatant 1 to an evaporating dish, add to it 2-3 ml of 2*N* H_2SO_4 and evaporate the solution until dense white fumes of H_2SO_4 are evolved (to near dryness). Allow the mixture to cool and again add to it 1 ml of 2*N* H_2SO_4. Stir the mixture thoroughly, centrifuge, and separate precipitate 2 from supernatant 2.

Precipitate 2: lead sulphate; analyze as described in *P* 4.

Supernatant 2: Bi^{3+}, Cu^{2+}, Cd^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+}, PO_4^{3-}; analyze as described in *P* 5 et seq.

4. Confirmatory test for lead ions. Wash precipitate 2 with hot water, transfer it to an evaporating dish, and add 2-3 ml of KOH or NaOH solution. Heat the mixture to boiling and centrifuge. Add to the solution 2*N* H_2SO_4 until the solution is acidic. The appearance of a white precipitate confirms the presence of lead.

5. Separation of bismuth, copper, and cadmium ions from cations of the other metals. Pass hydrogen sulphide into supernatant 2 until the sulphides are completely precipitated. Centrifuge the suspension and separate precipitate 3 from supernatant 3.

Precipitate 3: sulphides of bismuth, copper, and cadmium; treat as described in *P* 6.

Supernatant 3: salts of Fe^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, PO_4^{3-}; analyze as described in *P* 10 et seq.

6. Separation of bismuth ions from copper and cadmium ions. Wash precipitate 3 with hot water, transfer to an evaporating dish. Add 3-5 ml of 2*N* HNO_3 solution; heat the mixture to boiling and boil gently until all the black particles disappear. If a residue (sulphur) remains, centrifuge the mixture. Discard the residue and add to the solution concentrated ammonia solution to make it strongly alkaline. The formation of a precipitate of $Bi(OH)_2NO_3$ indicates the presence of bismuth ions. A blue coloration of the solution shows that copper is present. Centrifuge the suspension and separate precipitate 4 from supernatant 4.

Precipitate 4: basic bismuth salt; analyze as described in *P* 7.

Supernatant 4: cadmium- and cupri-ammonia complex ions; analyze as described in *P* 8 and *P* 9.

7. Confirmatory test for bismuth ions. Wash precipitate 4 with hot water and add to it an alkaline stannite solution (prepared as described in Sec. 80). The presence of bismuth ions is confirmed if the precipitate turns black.

8. Confirmatory test for copper ions. Acidify a portion of supernatant 4 with acetic acid to make the solution acidic and add a few drops of $K_4[Fe(CN)_6]$. The presence of copper is confirmed by the formation of a red-brown precipitate.

9. Test for cadmium ions. To another portion of centrifugate 4 add 4*N* HCl solution until the solution is acidic to litmus and pass hydrogen sulphide into it. After making sure that precipitation is complete, centrifuge the mixture and separate the solution from the precipitate. To the resultant clear supernatant add 2*N* NH_4OH solution until the mixture is just alkaline and pass in hydrogen sulphide once more. The presence of cadmium ions is indicated by the formation of a yellow precipitate.

10. Removal of hydrogen sulphide. Boil supernatant 3 to remove hydrogen sulphide (test with a piece of filter paper moistened with lead acetate, see Sec. 62, *P* 4). Add 1 or 2 drops of bromine water and boil the solution to remove bromide ions. Dilute the solution with 5 ml of water.

11. Test for iron ions. To 0.5 ml of the solution obtained above add 2 or 3 drops of $K_4[Fe(CN)_6]$. The presence of iron ions is indicated by the appearance of a blue precipitate or blue coloration of the solution.

12. Test for nickel and cobalt ions. If the solution contains iron, add to 0.5 ml of the solution 2 or 3 small crystals of NaF or KF. Divide the solution into two equal portions. To one of them add NH_4OH solution to make the solution alkaline and then 3-5 drops of dimethylglyoxime solution. The presence of nickel ions is indicated by the appearance of a bright red precipitate or red coloration of the solution. To the other portion of the solution add $ZnSO_4$ and $(NH_4)_2[Hg(SCN)_4]$ solutions (see Sec. 62, *P* 7). The formation of a blue precipitate indicates the presence of cobalt ions.

13. Test for manganous ions. Prepare a mixture consisting of 1 ml of 0.1*N* $AgNO_3$ solution, 1 ml of 2*N* HNO_3, and a pinch of sodium bismuthate and add to it 2 or 3 drops of

supernatant 3. Shake the mixture for 1-2 minutes. In the presence of manganous ions a purple solution will be formed due to permanganate ion.

14. Test for chromic ions. To 1-2 ml of supernatant 3 add small crystals of $(NH_4)_2S_2O_8$ and heat the mixture to boiling. The formation of a yellow solution indicates the presence of chromic ions.

Then carry out a confirmatory test for chromic ions. Prepare a mixture of H_2O_2, $2N$ H_2SO_4, and ether. Add to it a few drops of the yellow solution obtained above and immediately shake the mixture vigorously and then allow it to settle. The appearance of a blue coloration confirms the presence of chromic ions.

15. Test for phosphate ion. To 0.5 ml of supernatant 3 add 1 ml of $2N$ HNO_3 solution and 1 ml of $(NH_4)_2MoO_4$ solution. Boil the solution for 1-2 minutes. A yellow precipitate will appear if phosphate ions are present.

16. Test for zinc and aluminium ions. To a portion of supernatant 3 add NaOH or KOH until the solution is strongly alkaline. Heat the mixture to boiling and centrifuge. Discard the precipitate containing insoluble hydroxides of other metals and test for aluminium and zinc in separate portions of the solution.

Test for aluminium ion. To 2 or 3 drops of the above solution add 1 per cent Alizarin-S reagent and CH_3COOH a drop at a time until the violet colour disappears and then one more drop of CH_3COOH. In the presence of aluminium the solution will turn red. Aluminium ions can also be detected by precipitation of aluminium hydroxide, $Al(OH)_3$, (see Sec. 55, *P* 1).

Test for zinc ion. Acidify 0.5 ml of the alkaline solution obtained above with acetic acid to make the solution acidic and pass hydrogen sulphide into it. The formation of a white precipitate indicates the presence of zinc ions.

PART TWO
QUANTITATIVE INORGANIC ANALYSIS

CHAPTER XXIV

General

115. The Scope of Quantitative Analysis

Quantitative analysis is the section of analytical chemistry concerned with determining the quantitative composition of substances.

Like qualitative analysis, quantitative analysis developed and improved along with industrial progress. Quantitative determination of the composition of raw materials, fuel, intermediates, and finished products in industry is an indispensible component of production control in the metallurgical and chemical industries.

To analyze a sample quantitatively, it is necessary to know its qualitative composition which is the starting point for choosing the method of determining the contents of its individual components. For example, in the absence of iron, aluminium can be determined quantitatively in any of its compounds by direct precipitation of the aluminium ion from solutions of its salts with ammonium hydroxide; but in the presence of iron, quantitative determination of aluminium is much more complicated.

In most cases quantitative analysis employs the same chemical reactions as qualitative analysis. For instance, Cl^- ions are easily detected in solutions by the formation of an acid-insoluble precipitate of AgCl. The same reaction can be employed for determination of the content of Cl^- ions in solution. For instance, addition of an excess of silver nitrate to a solution containing chloride ions (acidified with nitric acid) will precipitate the chloride ions practically comple-

tely as insoluble AgCl. Knowing the mass of the resulting precipitate, the amount of chloride ions in the solution can be calculated. This method is called *gravimetric analysis.*

The same determination can be made in another way: an $AgNO_3$ solution of known concentration is added to the solution containing the Cl^- ions until all the chloride ions are completely precipitated. Knowing the volume of $AgNO_3$ solution used for the precipitation, the amount of Cl^- ions contained in a definite volume of the unknown solution is calculated. Such is the method known as *volumetric analysis.*

Sometimes the colour reactions used in qualitative analysis are utilized to determine the amount of some of the components in a substance. For example, ferric ions, Fe^{3+}, form a complex compound with CNS^- ions, which colours the solution red. Independent of the amount of thiocyanate ion added, the intensity of colouring depends on the amount of iron in the solution. By comparing the colour intensity of several solutions of known concentration with that of the unknown solution, the concentration of iron in the latter can be determined. This is the *colorimetric method* of quantitative analysis.

Analysis of gases consists essentially in measuring the volume of the gas being determined or the volume of gaseous substances obtained as a result of various chemical reactions. This divison of quantitative analysis is called *gas analysis.*

GRAVIMETRIC ANALYSIS

CHAPTER XXV

Introduction to Gravimetric Analysis

116. General Principles

Gravimetric analysis is based on precipitating the unknown component of the substance under test from solution as an insoluble compound of known chemical composition. The content of the component is then calculated from the weight of the resulting precipitate.

The precipitate is often ignited before weighing, to decompose and convert it into a substance of a different composition which is, for some reason or other, more convenient to weigh. For example, the amount of iron in solutions of its salts is determined by precipitating $Fe(OH)_3$ with ammonia solution. When ignited, ferric hydroxide loses water and changes into the oxide Fe_2O_3, which is weighed. For this reason in gravimetric analysis a distinction is made between the precipitated and weighed forms of the substance. In the above example $Fe(OH)_3$ is the precipitated, and Fe_2O_3, the weighed form.

Sometimes the precipitated and the weighed forms coincide. For instance, Ba^{2+} ion is precipitated from solution with sulphuric acid as $BaSO_4$ and is weighed also as $BaSO_4$. Ignition does not alter its chemical composition. In the majority of cases, however, the precipitated form differs in chemical composition from the weighed form.

The requirements imposed on the precipitated and the weighed forms of substances are different.

A substance in the *precipitated form* should:

(1) possess low solubility, i.e., a low solubility product;

(2) form large crystals to avoid clogging filter pores (this makes for rapid filtration), minimize adsorption of foreign matter from the solution, and facilitate removal of impurities by washing. Finely crystalline precipitates pass freely through the filter pores, which is inadmissible in gravimetric analysis. Amorphous precipitates, especially jelly-like ones, such as $Al(OH)_3$, are apt to adsorb considerable amounts of extraneous matter from the solution and are difficult to wash. Besides, amorphous precipitates take a long time to filter;

(3) change readily and completely into the weighed form.

A substance in the *weighed form* should:

(1) have a definite chemical composition, from which the amount of the unknown component can be calculated;

(2) be chemically stable, i.e., have low hygroscopicity, not absorb carbon dioxide, and not be oxidized or reduced when strongly heated.

These requirements determine the choice of chemical compounds for precipitated and weighed forms, as well as the conditions of their precipitation.

CHAPTER XXVI

Apparatus for Gravimetric Analysis

117. Analytical Balance and Its Use

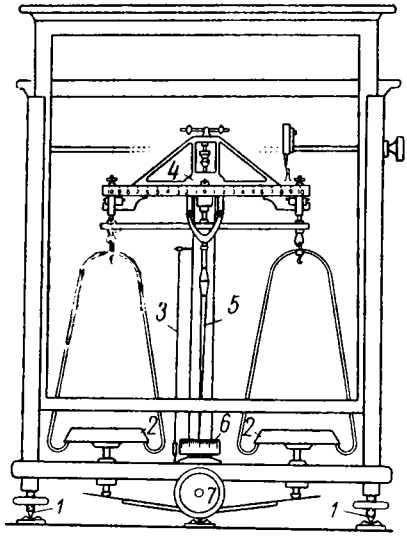
Two types of balances are in use in chemical laboratories for precise weighing: the ordinary analytical balance and the damped balance.

Design of analytical balance (Fig. 13). With a load of not more than 200 g, weighings can be made on the analytical balance to the nearest 0.0002 g. To protect the balance from dust and to prevent air drafts from affecting beam deflection during weighings, the balance is enclosed in a glass-fitted case with a sliding front door which lifts upward and doors in its side. The side doors are used during weighings, the front door being raised only when absolutely necessary.

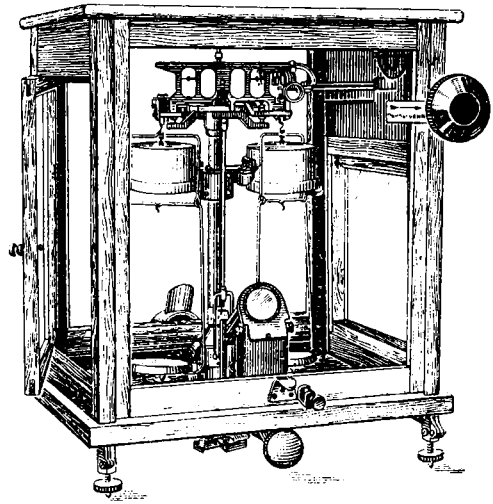
The most important part of the analytical balance is beam *4* which is an equal-armed lever furnished with long vertical pointer *5*, by the deflection of which the movement of the beam can be judged. The lower end of the pointer swings in front of scale *6* with divisions for reading the amplitude of swing. The scale has a zero line in the middle and 10 divisions on either side of it. When the beam is horizontal (the pans are balanced) the pointer should rest opposite the zero line of the scale.

The beam has agate knife edges at its extremes, supporting stirrups from which balance pans *2* are suspended. Another agate or steel knife edge is fixed exactly in the middle of the beam on its bottom side. This knife edge faces downwards and supports the beam.

To prevent the knife edge from becoming dull under the weight of the beam and pans, the balance is equipped with a special device called an arrest. It bears the weight of the beam and pans when weighing is not being done and the balance is at rest. The arrest is operated by means of milled knob *7* underneath the base plate in the middle and in front of the balance (sometimes the arrest knob is at one side of the balance). To put the balance in its operating position the arrest is lowered by rotating the knob, which releases the beam and sets its knife edges on their cushions. To stop the movement of the beam, the knob is rotated in the oppo-



(a)



(b)

Fig. 13. Balances

a — analytical; *b* — damped; *1* — supports; *2*—pans; *3* — plumb line; *4* — beam; *5* — pointer; *6* — graduated scale; *7* — knob

site direction as far as it will go, which raises the arrest. A balance with its arrest raised is said to be arrested. When not in use and during loading or unloading of the pans, the balance should be arrested.

To check whether the object being weighed and weights balance each other, rotate the arrest knob slowly and smoothly with the left hand; as soon as the pointer begins to swing, turn the arrest knob at a gradually increasing speed as far as it will go.

For determining thousandths and ten-thousandths of a a gram, the beam has a scale straddled by a special bent wire weight called a rider. The rider is moved by means of a special carrier rod arranged above the beam. The carrier is moved along the beam by the knob on the end protruding from the balance case at the right. On its left end the carrier has a hook by means of which the rider can be caught up and moved to the desired scale division.

The pans are considered balanced if the beam, brought out of its horizontal position, returns after a few swings to its initial position with the pointer opposite the scale zero. If the beam stops in an inclined position, the pans are not balanced and weights should be added or removed.

With the analytical balance operating properly, the results of several weighings of the same object should always be the same. Besides, if the balance is correctly aligned, its beam should retain its initial equilibrium position when equal masses are placed on the pans.

The sensitivity of the balance is measured by the deflection of the pointer upon insignificant overloading. A balance is considered sufficiently sensitive for analytical work if an overload of 1 mg deflects the pointer 3-5 divisions.

Installing the balance. The balance should be installed in the weighing room on a sturdy wooden or marble shelf supported by brackets fixed to a main wall, in a strictly vertical position checked with the aid of plumb line *3*. This is achieved by means of two front supports *1*, the upper parts of which are threaded. The supports are placed on special blocks, flat underneath and cup-shaped on top.

Sets of weights. For precise weighings analytical weights are used, kept in a special box with recesses for each weight (Fig. 14).

A set of analytical weights consists of the following weights: 100, 50, 20, 10, 5, 2, 2, and 1 g. Besides, the set includes the smaller weights: 500, 200, 200, 100, 50, 20, 20, 10, and 10 mg.

The weights from 500 to 10 mg are flat pieces of metal with a bent-up edge or corner. They are sometimes made of

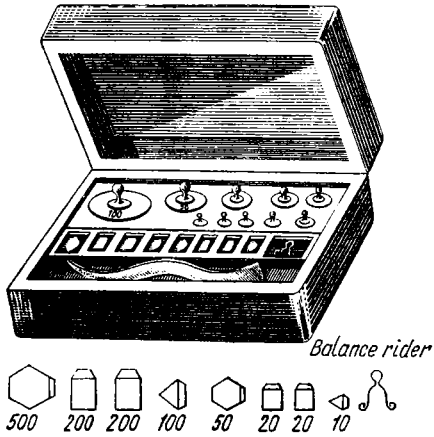


Fig. 14. Box of analytical weights

different shapes; a very popular assortment is: hexagons for 500 and 50 mg, squares for 200 and 20 mg, and triangles for 100 and 10 mg.

It should be noted that the masses of weights of the same denomination, even in the same set, may begin to differ after some time owing to unequal wear. To reduce the possible weighing error, always use the same set of weights. Place weights on the balance pan in the same succession as they lie in the box and always return each to its proper place.

Handle weights only with the forceps furnished with the set. Grasp weights of 1 g and more by their long upper end, and smaller weights (smaller than 1 g), by their bent-up edge or corner. Never use the forceps for other purposes.

Rider. Thousandths and ten-thousandths of a gram are determined with the rider (Fig. 14) which is made of aluminium or platinum wire. The rider weighs 0.01 g. By means

of the carrier, the rider can be moved along the upper scale of the balance, fixed to or marked on the beam and having 10 large divisions on each side of the middle; each large division is subdivided into five smaller divisions (Fig. 15). When the rider is on the zero division, it has no effect on the balance of the pans. Placing it on the tenth division of the right-hand beam arm is equivalent to adding a 0.01 g weight to the scale pan.

Each large division of the upper scale (on the beam) corresponds to 0.001 g, and each small division, to 0.0002 g.

Fig. 15. Beam scale

Hence, by moving the rider to the right of zero, the load on the right-hand pan can be increased a minimum of 0.0001 g and a maximum of 0.01 g. On the other hand, moving the rider along the left-hand side of the scale increases the load on the left-hand pan. Usually the rider is moved only along the right-hand side of the scale.

Rules in weighing. To keep the balance in working order and to obtain accurate results the following rules should be observed:

1. Sit squarely in front of the balance when weighing.
2. Keep no objects inside the balance case except beakers with calcined calcium chloride (to absorb moisture), which should be placed in the back corners of the case. Keep the balance meticulously clean. If anything gets spilled on the pan or the case bottom, sweep it out immediately with a soft brush. Wipe the pans with chamois leather; never use liquids of any kind to clean them.
3. Align the balance strictly vertical by its plumb line. Do not move the balance after alignment, otherwise it will have to be readjusted.
4. When weighing, open only the side doors of the case; do not raise its front door.
5. Never place the substance being weighed directly on the pan or on paper. Weigh solids on a watch glass or in a beaker, and volatile and hygroscopic substances and liquids

in weighing bottles. Glassware used for weighing should be clean and dry.

6. Objects being weighed should have the same temperature as the weighing room. To ensure this, keep them in a desiccator in the weighing room for at least 15 or 20 minutes before weighing.

7. Never load the balance above its maximum load (200 g).

8. Change the load on the balance only after fully arresting it.

9. Remove or add substance being weighed only outside the case.

10. When observing pointer deflections, keep the case doors shut.

11. Never touch weights, pans, or balance beam. Handle weights only with plastic-tipped forceps.

12. Place weights on the right-hand pan, arranging them in the centre to avoid skewing of the pan, which may distort the reading.

13. Open the box of weights only when weighing.

14. Before and after using, keep the rider on the carrier hook clear of the beam scale.

15. After finishing weighing, move the carrier inside the case.

16. Having finished weighing, arrest the balance and check your record of the results. Without opening the case doors, remove the rider from the beam scale using the carrier rod, open the right-hand case door, replace the weights in their places in the box, open the left-hand case door, remove the object weighed from the scale pan and close the case door.

17. When you have finished weighing, clean the balance with a brush or a piece of chamois leather to remove possible spillage or other dirt.

If the balance goes out of order, consult the instructor.

Determination of zero point. The zero point of a balance should be established before each weighing. The zero point is the scale division at which the pointer comes to rest after the beam has stopped oscillating, with no load on the pans. For exact readings of pointer deflections, scale *6* with 20 divisions is fixed to the bottom of the supporting column. Each fifth division is slightly longer than the rest, to faci-

litate reading the pointer deviations from the middle (zero) division.

The zero point is determined as follows: carefully release the arrest device to make the beam swing smoothly; neglect the first two deflections, and beginning with the second period of swinging write down the value of each pointer deflection to the left and to the right of the zero division. Read off an even number of deflections in one direction and an odd number in the other. The deflection of the pointer from the middle position in both directions should be not less than three and not more than seven divisions. If the deflections are greater or smaller than these, stop the beam with the arrest and carefully release it again.

After three or five readings of pointer deflections in one direction and two or four in the other, find the average deflection in each direction, subtract the smaller deflection from the larger one and divide the difference by two. The result corresponds to the position of the zero point of the balance.

Calculation of Zero Point (Example)

Deflection of pointer to the left	*Deflection of pointer to the right*
6.0 divisions	5.0 divisions
5.5 divisions	4.5 divisions
5.0 divisions	
Average 5.5 divisions	Average 4.7 divisions

Subtracting the smaller deflection (4.7) from the larger (5.5) and dividing the difference by two, we get 0.4. Hence, the zero point is 0.4 divisions to the left of the scale zero [1].

Directions for weighing. Before starting to weigh, make sure that the inside of the balance case is clean, that the rider is on the carrier hook and that all the weights are in their proper places in the box. Weighings on an analytical balance should be made in the following order:

(1) determine the zero point of the balance as described above;

[1] If the zero point of the balance differs sharply from the scale zero (discrepancy of 2-3 divisions), consult your instructor to have the balance put in order.

(2) open the left-hand case door and place the object to be weighed on the scale pan;

(3) close the left-hand door, open the right-hand door and place the weights on the pan, from larger to smaller.

By way of example let us consider the weighing of a watch glass.

Find the approximate mass of the glass by weighing it on a rough balance. Suppose it equals 9.8 g. Place the watch glass on the left-hand pan of the analytical balance and a 10-g weight on the right-hand pan. Turn the arrest knob slightly with the left hand, watching the pointer. If the pointer is deflected sharply, return the arrest knob to its initial position without turning it any further. If the pointer is deflected, say, to the left, signifying that the scale pan with the weights is heavier, remove the 10-g weight with the forceps and return it to its place in the box, replacing it on the scale pan with weights totalling 9 g. Turn the arrest knob slightly, again watching the pointer. If the pointer now swings to the right, add the 500-mg weight and again turn the arrest knob. Continue adding or removing weights in this way down to 10 mg, inclusively. If adding the 10-mg weight made the pointer swing to the left of the zero point, remove the 10-mg weight, close the right-hand door of the case and use the rider. First place the rider on division 5 and rotate the arrest knob as far as it will go. If the pointer swings right of the zero point, move the rider to the right. If the pointer swings left, move the rider in the same direction. Always arrest the balance before moving the rider.

Continue shifting the rider until a position is found where the pointer swings equally to the right and left of the zero point established before weighing as described above.

Having finished weighing, write down the mass of the object found. First count up and record the mass of the weights missing in the box and the position of the rider. Then check the record while removing the weights from the scale pan (beginning with the largest weight) and returning them to their places in the box. Then hook the rider off the beam and remove the object from the scale pan.

After the receptacle (in our case the watch glass) has been weighed and its mass recorded in the notebook, weigh the sample of the substance to be analyzed.

Suppose the watch glass weighs 9.4172 g and a sample of about 0.5-0.7 g is to be taken for the analysis. Place weights totalling about 9.4 ± 0.5 g on the right-hand pan of the balance. Place about 0.5 g of the substance on the weighed watch glass, set the watch glass with the sample on the left-hand pan and turn the arrest knob a little. If the pointer swings right of the zero point, the receptacle with the sample is heavier than the weights. If it swings left, the sample is too small and some more material should be added.

Material may be added to or removed from the sample only outside the balance case.

If the watch glass with the sample is heavier than the weights, check to see whether too much material has been added. In the case under consideration add a 200-mg weight to the right-hand pan. If after this the pointer swings left of the zero point, the amount taken for the sample is correct. To find its exact weight, remove the 200-mg weight from the right-hand pan and add smaller weights until the pans are balanced, in the same way as when weighing the watch glass.

118. Damped Balance and Its Use

Design of balance. Weighing can be done much more rapidly on an АДВ-200[1] damped balance (see Fig. 13*b*).

This balance is furnished with dashpots, devices to stop the swinging of the balance pointer very quickly, and has an automatic device for hanging fractional weights totalling from 10 to 990 mg in mass on the beam and removing them from it. Besides, this balance has a special optical attachment with an illuminated screen for reading off the position of the pointer.

Each dashpot consists of two aluminium cylinders, one fitting into the other. The outer cylinder is fixed rigidly to the vertical column of the balance. The inner cylinder is suspended from the balance stirrup by means of a hook. Thus, the dashpots are arranged above each of the scale pans.

If the arrest is carefully released, the inner dashpot cylinders begin to swing together with the balance beam and pans.

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[1] Soviet code mark standing for 'Automatic Damped Balance', maximum load 200 g.

They should rise and fall freely without touching the walls of the outer cylinders; then their movement causes an air drag, so that after two or three swings the pointer comes to rest at the scale division corresponding to the point of equilibrium.

The right arm of the balance beam has a horizontal plate fixed to it, on which small ring-shaped weights can be seated. Each weight hangs on a special hook above the plate. By means of a system of levers operated by a double-disc hand knob, any of the weights can be placed on the plate or removed from it. The set includes eight weights of mass 500, 200, 100, 100, 50, 20, 10, and 10 mg.

The knob is arranged outside the case in its upper right-hand part and consists of two concentric two-way rotating discs with figures engraved on them. Weights of mass totalling 100, 200, 300 . . ., 900 mg are placed on the plate by rotating the outer disc (equivalent to placing 0.1, 0.2, . . ., 0.9 g on the right-hand pan) and weights of mass totalling 10, 20, 30, . . ., 90 mg, by rotating the inner disc (equivalent to placing hundredths of a gram on the right-hand pan).

An index in the form of an arrow is engraved next to the discs to indicate the total mass of the weights placed on the plate. For example, if number 6 on the outer disc and number 4 on the inner one are opposite the index, this means there is altogether 640 mg or 0.64 g on the plate.

Milligrams and tenths of milligrams, i.e., thousandths and ten-thousandths of a gram are determined on this balance by the deflection of the pointer, which is read off with the optical attachment. Its screen is illuminated by a lamp installed on the back wall of the balance case, which is switched on automatically (through a transformer) when the arrest is released.

The damped balance has a number of advantages: it eliminates counting and reading off pointer deflections and calculating the zero point; no small weights need be placed on the scale pans and no rider manipulation is required The damped balance is of the same order of precision as the ordinary analytical balance.

Weighing technique. When weighing on a damped balance, the following rules should be observed:

1. Connect the illuminator to supply mains of appropriate voltage with a cord and plug.

2. Adjust the position of the zero point as follows: without opening the case doors, turn the arrest knob carefully as far as it will go. The electric light goes on automatically and illuminates a magnified image of the microscale on the screen. As the pointer swings, the image of the microscale moves across the screen, but owing to the dashpots the pointer stops very soon. When the balance is not loaded, the scale zero should coincide exactly with the vertical line on the screen. This can be achieved by rotating an adjustment screw situated outside the case above the arrest knob.

3. Place the object to be weighed on the left-hand pan and weights from the box, representing a whole number of grams, on the right-hand pan.

4. Close the case door and to determine tenths of a gram manipulate the outer disc to hang weights of 500, 200, and 100 mg successively on the beam plate. Check each time to see in which direction the pointer swings. Before each turn of the disc, i.e., before removing or hanging any weight on the plate, the balance must be arrested.

Set weights of hundredths of a gram similarly with the inner disc.

5. Read thousandths and ten-thousandths of a gram off the microscale. For this purpose turn the arrest knob as far as it will go and after the pointer stops swinging take the reading indicated by the vertical line on the screen scale. The large divisions of this scale are thousandths and the small ones, ten-thousandths of a gram. The figures on the scale have plus or minus signs before them. The plus sign indicates that the reading should be added to the mass of the weights on the balance, and the minus sign indicates that this value should be subtracted[1]. For example, if weights totalling 18.64 g are on the balance and the screen reading is 5.7 mg, i.e., 0.0057 g, the mass of the object is 18.6457 g if the reading is positive, or $18.64 - 0.0057 = 18.6343$ g, if the reading is negative.

6. After the weighing is over, record the result obtained and remove the object and weights from the balance. To remove the small weights from the beam, turn the disc knobs to align the zero divisions of both discs with the index.

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[1] It is good practice to use only the plus readings of the scale.

119. Laboratory Ware and Other Equipment

Beakers. Thin-walled lipped beakers of various size, mainly 100, 200, and 400 ml, are used in gravimetric analysis.

Funnels. Regular 60° conical funnels are recommended for filtering.

Three types of funnels are used for recrystallizing salts and other substances: (a) short-stem funnels, (b) funnel heaters, (c) porcelain Buchner funnels.

The funnel heater (Fig. 16) is a copper funnel with double walls, the annular space between which can be filled with water. It is used to keep liquids hot while filtering. The funnel has a side branch beneath which a Bunsen burner can be placed to heat the water between the walls. An ordinary glass funnel with a filter paper is inserted in the funnel heater. Electric funnel heaters are especially convenient for filtering readily flammable liquids.

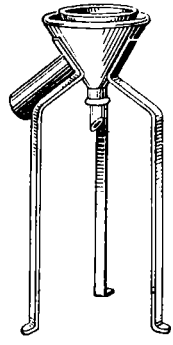


Fig. 16. Funnel heater

Suction-funnel (Fig. 17). The Buchner porcelain suction funnel *1* has a perforated bottom. It is inserted in thick-walled suction flask *2* through a one-holed rubber stopper.

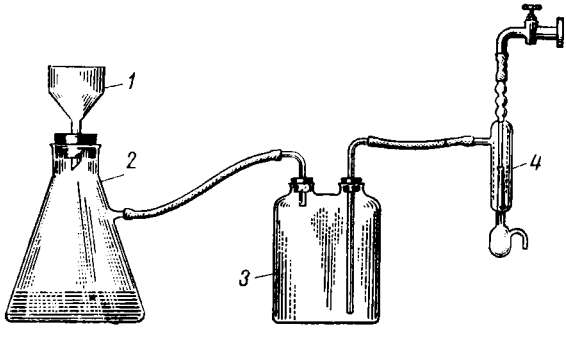


Fig. 17. Suction apparatus

1 — Buchner funnel; *2* — stout glass flask; *3* — safety bottle; *4* — water-jet pump

During filtration the flask is connected by means of a thick-walled rubber tube via intermediate safety flask *3* to vacuum

or water-jet pump *4*. Two circular discs of filter paper are placed on the perforated bottom of the funnel, the diameter of the lower disc being almost equal to that of the filter bottom and the diameter of the upper one, 2-3 mm larger. To cut out discs of the desired size place filter paper on the funnel and press it lightly with the palm; this gives an impression of the funnel perimeter. Cut out the paper with a pair of scissors exactly along the impression, and then trim the filters to fit the bottom of the funnel. Place the filter paper accurately in the funnel, pour in some distilled water, connect the flask to the vacuum pump, and start filtering.

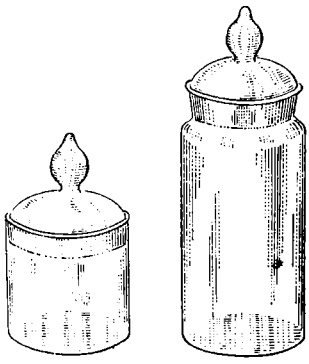


Fig. 18. Weighing bottles

Wash bottle. A 500-700 ml wash bottle (see Fig. 7) is needed for quantitative analysis.

Glass stirring rods should be 15-20 cm long and 2-3 mm thick; thicker rods are inconvenient.

Watch glasses. It is good practice to have watch glasses of two sizes available: 4-6 cm in diameter for taking samples and 9-11 cm in diameter for covering beakers or funnels (convex side downwards).

Weighing bottles (beakers with ground-in or ground-on covers). Weighing bottles (Fig. 18) are used as receptacles for weighing liquids and substances that are unstable in the air. The most convenient sizes of weighing bottles are: about 35 mm in dia and 50 mm high; about 45 mm in dia and 25 mm high. Weighing bottles are used for determining moisture content, for weighing liquids, and for weighing substances which must be isolated from the ambient air (e.g., sodium hydroxide).

Porcelain crucibles (Fig. 19) are used for igniting precipitates. The most convenient are low wide-bottomed crucibles.

Crucible tongs. Crucibles are handled with special tongs with flat upturned ends (Fig. 20). Before using, the ends of the tongs should be cleaned by heating strongly over a Bun-

sen burner. Crucibles should be grasped with the tongs by their edges (never girth the crucible with the tongs).

Clay triangles. For heating, porcelain crucibles are nested in triangles made of clay tubes set on spliced wire (see Fig. 19). Rustless steel wire is recommended for this purpose.

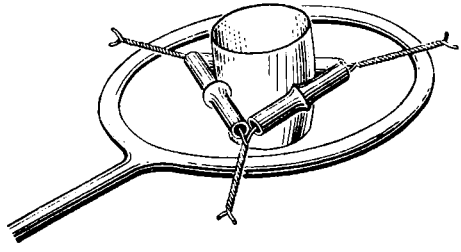


Fig. 19. Porcelain crucible and clay triangle

Desiccators. Before weighing, the substances whose mass is to be determined and the receptacles must acquire the temperature of the weighing room. Since heated or ignited substances absorb water vapours from the surrounding air

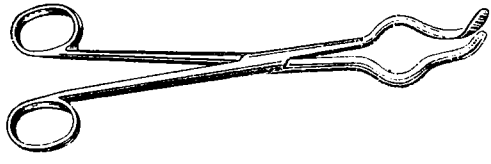


Fig. 20. Crucible tongs

on cooling, which increases their mass, they should be cooled in vessels called desiccators. A desiccator (Fig. 21) is a thick-walled glass bowl narrower at the bottom and covered with a ground-glass lid. The ground edges of the desiccator are coated with a thin layer of petrolatum (vaselin). The bottom compartment of the desiccator is filled with a drying agent (*desiccant*) e.g., freshly calcined calcium oxide, calcined calcium chloride, or concentrated (not less than 85 per cent) sulphuric acid. The acid absorbs moisture much more intensively than calcium oxide or calcium chlo-

ride. However, desiccators that have to be carried from place to place during work are more convenient if filled with freshly calcined lime or calcium chloride.

A porcelain tray (see Fig. 21*a*) with holes for keeping crucibles in position is placed in the desiccator above the drying agent. Weighing bottles, watch glasses, etc. can also be placed on the tray. The tray is often made with legs

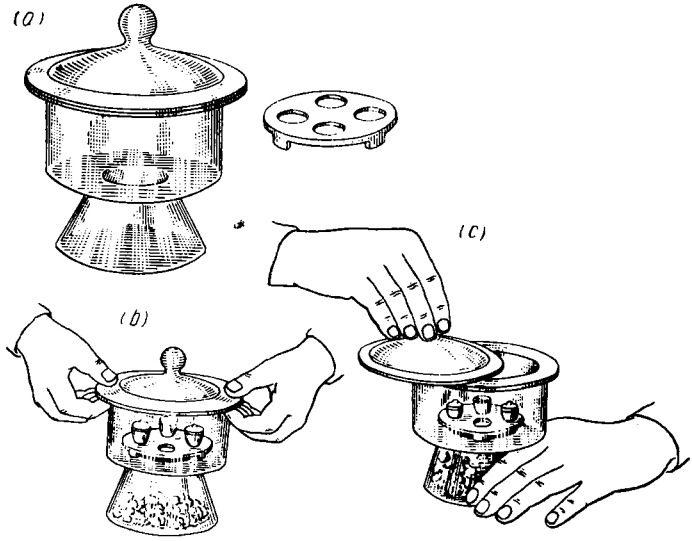


Fig. 21. Desiccator and tray
a — general view; *b* — carrying the desiccator; *c* — opening the desiccator

4-5 mm high on its bottom side so that the crucibles are by all means clear of the layer of desiccant. The latter should be replaced from time to time.

When carrying the desiccator from place to place, it should be taken in both hands with the thumbs pressing firmly down on the lid (see Fig. 21*b*). When opening the desiccator, do not lift the lid vertically. Hold the desiccator with the left hand and move the lid sideways with the right hand (Fig. 21*c*). Set the desiccator lid on the table inside up.

Owing to the hygroscopicity of the drying agent, the desiccator should be opened only for short periods of time.

Drying cabinets. Laboratories usually use electric drying cabinets with thermostat control for maintaining constant temperatures up to 250°C (Fig. 22). They have double walls with nickeline or nichrome elements between them.

The drying cabinet has two apertures at the top: one to accommodate a stopper carrying a thermometer for measuring the temperature inside the cabinet, and the other serving as an exhaust for water vapours and hot air from the cabinet.

Inside the drying cabinet are metal shelves with round holes about 1 cm in diameter, on which weighing bottles, beakers, watch glasses, and other laboratory ware can be placed.

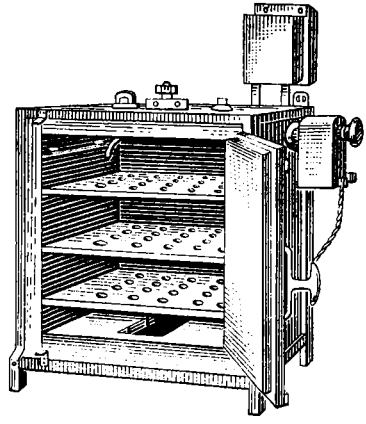
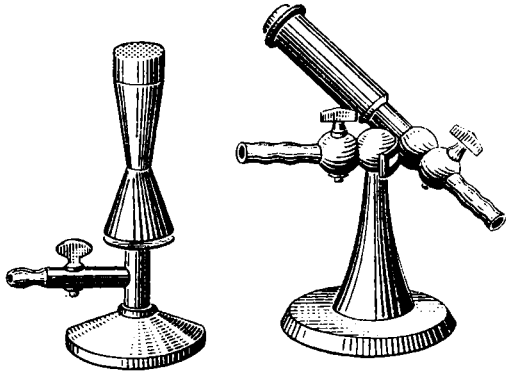


Fig. 22. Electric drying cabinet

Funnels are inserted into the holes in the shelves. Drying cabinets are fixed to a wall or set up on a table on a slab of some heat-insulating material.

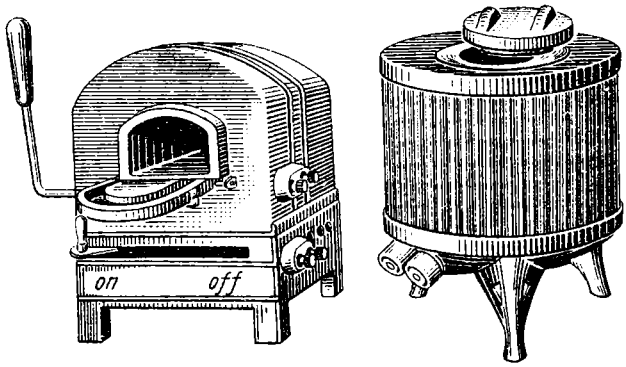
Burners. Apart from conventional Teclu burners, analytical laboratories use burners of other kinds by means of which higher temperatures can be attained. These include the Meker burner (Fig. 23*a*) and blowpipe (Fig. 23*b*), furnished with a special air supply system, which gives a higher flame temperature. The heating temperature of the Teclu burner is up to 700°C, the Meker burner gives 800°C, and the blowpipe develops temperatures up to 900°C.

Electric heaters. The following heating devices are the most popular in chemical laboratories: (a) drying cabinets with temperature control (Fig. 22); (b) muffle (Fig. 24*a*) and crucible (Fig. 24*b*) furnaces in which temperatures up to 1,200°C can be obtained; (c) electric hot plates; (d) water



(a) (b)

Fig. 23. Burners
a — Meker-type; b — blowpipe



(a) (b)

Fig. 24. Furnaces
a — muffle; b — crucible

baths (Fig. 25). To keep electric appliances in good working order the following rules should be observed:

(a) plug appliances into mains only of the voltage indicated on their nameplate (electrical appliances are usually designed for 127 or 220 V);

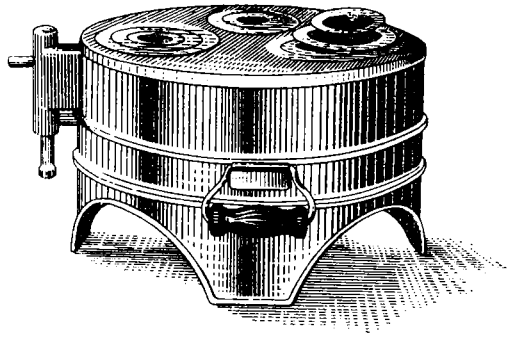


Fig. 25. Electrically heated water bath

(b) set electrical appliances on a thick asbestos plate or a sheet of heat-insulating material;

(c) keep appliances clean;

(d) when using water baths not furnished with automatic water feed, take care to refill them with water in time and never heat them without water;

(e) switch appliances off when not in use.

Muffle furnaces. Electric muffle furnaces are made of fire clay. They have a coil of thick nickeline or constantan wire and a rheostat for regulating the temperature of heating. Connect the furnace to supply mains with the rheostat fully in. Subsequently, decrease the resistance gradually as the furnace grows hotter by shifting the rheostat handle. This will warm the furnace up gradually and prevent overheating the coil. While heating, keep the furnace door closed.

Besides the apparatus and laboratory ware mentioned above, quantitative analysis requires the same equipments as qualitative analysis, namely, stands, flasks, asbestos gauzes, etc.

CHAPTER XXVII

Gravimetric Techniques

120. General Directions for Laboratory Work

The laboratory working table and all the apparatus should be kept clean and in order. Glassware can be considered clean only if water wets its entire inside surface without leaving drops on its inside walls. The outer surface should be wiped dry with a clean towel, but inside surfaces of glassware should never be touched with a towel; these surfaces are left wet or are dried in a drying cabinet. During the analysis mark beakers, flasks, and other glassware with a wax (Chinagraph) pencil and cover them with a watch glass or a piece of filter paper.

Before starting an analysis, familiarize yourself thoroughly with the procedure, write out a plan and prepare the reagents and glassware needed for the analysis. Use only very pure reagents, because contaminated reagents may constitute a serious source of error in analysis. Especially pure reagents are called chemically pure and denoted C.P.; analytical reagent (A.R.), pure (P), refined (ref.), and commercial grade reagents also indicate definite standards of purity of a chemical. Only chemically pure or analytical reagents are suitable for quantitative analysis.

In planning the work, make a note of the point at which the analysis can be interrupted. For example, do not start filtering unless the precipitate can be washed on the same day. A precipitate which takes a long time to settle should be thrown down towards the end of the work day and left standing overnight.

To save time, some operations may be carried out simultaneously. For example, filtering can be done while a crucible is being calcined; a sample can be weighed out for a new analysis while the crucible with the precipitate of a previous one is cooling, etc.

Never be in a hurry to finish any operation, because this may lead to an error or to loss of some of the substance.

All analysis data should be recorded immediately in the laboratory notebook, in a definite order.

121. Sampling

The weighed portions used for quantitative analysis are very small (see Sec. 127). To ensure that the results of analysis of the weighed portion reflect the quantitative relations between components in the entire sample as closely as possible, it is necessary to take a representative sample correctly. Samples delivered to the laboratory are usually homogeneous and in the form of a powder; sometimes they are

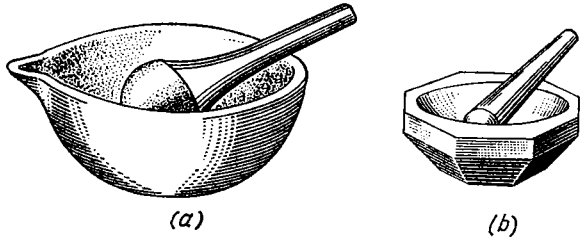


Fig. 26. Mortars
a — porcelain; *b* — agate

in the form of lumps. Lumps must be pulverized prior to taking an average sample. There are several methods of sampling. One of them is called quartering (used for sampling large lumps but also used on the laboratory scale). When sampling by this method the large lumps of the sample are broken into smaller ones which are then ground. The resulting material is arranged in an even layer not more than 2-3 cm thick in the form of a square on a sheet of paper. The square is divided diagonally into four triangles. The portions in two opposite triangles are discarded, and those in the other two are mixed and ground again. Then a square is formed once more and quartered. This procedure is repeated until 10-20 g of finely pulverized material is obtained.

The samples can be ground in mortars made of porcelain (Fig. 26*a*), agate (Fig. 26*b*), or steel depending on the hardness of the sample. Before using a mortar, wash it thoroughly and dry it in a drying cabinet. Put a thin layer of the substance to be ground in the mortar. Break the larger lumps by

striking them carefully with the pestle until they are of pea size, and then grind them with the pestle; transfer the ground material to a clean weighing bottle. The weighed portion for further analytical determinations is taken with a porcelain or metal spatula.

122. Dissolving of Samples

To dissolve the sample prepare a clean beaker appropriately marked with a Chinagraph pencil.

Transfer the weighed sample to the beaker by carefully overturning the watch glass on which it was weighed over the beaker so that most of the material falls off the glass. Wash the remaining traces of the sample into the beaker with a jet of water from the wash bottle.

If the material is soluble in water, use about 100-150 ml of water for this purpose. If the substance is soluble only in acids or alkalies and is likely to evolve gases while dissolving, treat it with the acid or alkali in a small beaker covered with a watch glass. After dissolving, wash all splashings off the watch glass into the same beaker with water. If the sample has to be heated to dissolve it, heat it on an asbestos gauze or in a water bath. To avoid spattering, do not allow violent evolution of gases or strong boiling. After the weighed portion has dissolved completely, dilute the resulting solution with water to 100-150 ml.

123. Precipitation and Completeness of Precipitation

After selecting the proper precipitant, read over the conditions of precipitating in the textbook, noting the temperature, reaction of the medium, etc.

Precipitating is usually done in beakers from hot solutions, because high temperature favours the formation of coarsely crystalline precipitates which are easier to filter. But do not heat the solution to boiling to avoid losses due to spattering. The precipitant solution is most often added in a thin stream, stirring constantly. Take care that the stirring rod does not touch the walls and bottom of the beaker and scratch them.

The ends of the rod should be well fused. It is good practice to have two stirring rods at hand. One of them should be tipped with a piece of rubber tubing 10-15 mm long. The rubber tubing should be drawn tightly onto the rod so that the end of the tubing is flush with the end of the rod. The rubber tip is used to remove traces of the precipitate adhering to the beaker walls. The rubber-tipped rod should not be used for stirring the solution. When precipitating, add a slight excess of precipitant (see Sec. 129) and check for completeness of precipitation.

In most cases the precipitate is left standing to settle for a long time. But sometimes this is harmful, e.g., in the case of amorphous precipitates which are of high absorptive power and pass readily into the colloidal state.

TEST FOR COMPLETENESS OF PRECIPITATION

In gravimetric analysis completeness of precipitation is checked somewhat differently than in qualitative analysis. Add a few drops of the precipitant carefully to the solution with the settled precipitate, letting them run down the beaker wall, and watch the drops as they run down. If no turbidity forms at the point the precipitant drops fall into the solution, precipitation is complete. It is good practice to recheck for completeness of precipitation before filtering.

124. Filtration and Washing of Precipitates

The best funnels for filtering are those of the shape of a regular cone (apex angle 60°), with a stem a little longer than the cone height. Funnels may be of different sizes; the most popular are funnels with a top diameter of 60 to 70 mm.

Filtering and washing the precipitate are the most important operations in gravimetric analysis; the accuracy of the results depends on how carefully these operations are carried out.

Filtering is done through paper filters or through porous-bottom crucibles or funnels.

Most precipitates are filtered with ash-free paper filters because the mass of ash remaining after ignition of such

filters is negligible. For example, the mass of the ash of one large filter paper (11 cm dia) is 0.0001 g.

If the filter ash is more than 0.1 mg, its mass should be subtracted from the mass of the precipitate.

Before starting to filter through a paper filter, make sure of the size and closeness of texture of the filter required.

Ash-free filters differ in diameter and texture. The most popular sizes are 5, 7, 9, and 11 cm in diameter. Select filter size according to the volume of precipitate rather than that of the solution to be filtered. The precipitate should occupy not more than one third of the filtering cone volume.

The texture of the filter affects the filtering rate. Filters are made in three grades: (a) coarse-texture, quick filtering, suitable for filtering amorphous precipitates (e.g. ferric hydroxide); (b) medium-texture for filtering most of the crystalline precipitates; (c) close-texture (also called baryta filters) which filter slowly and are used for separating finely crystalline precipitates, such as $BaSO_4$ and CaC_2O_4.

Filters are available in 100-sheet packages (with labels indicating the diameter of the filter paper and the mass of its ash. Each package has a coloured paper band glued on it, indicating the closeness of texture of the filter paper in the package: a red band indicates coarse-texture filters; a blue band, close-texture filters; and a white band, medium-texture filters. After selecting the filter paper of the required closeness of texture and size, select a funnel of such a diameter that the edge of the filter placed in it is 5-10 mm below its upper rim.

Fold the filter paper neatly and place it in the funnel, smoothing it out and wetting it with water; then press it firmly against the funnel walls with the right thumb to drive out any air bubbles between glass and paper. To make sure the filter paper is functioning correctly, fill it almost to the top edge with distilled water; the water should flow out of the funnel in a thin stream and should fill the stem quickly. If the water flows out slowly, drop by drop, take a new piece of filter paper and put it in the funnel correctly. An incorrectly placed filter paper will retard filtering. After the filter paper fits well in the funnel, insert the latter in a stand ring wrapped in a strip of white paper and place

a beaker below it to collect the filtrate. The bevelled end of the funnel stem should touch the beaker wall.

When filtering, first decant the clear supernatant liquid through the filter paper, pouring it down the stirring rod which should be held firmly against the lip of the beaker. This method of pouring off the clear liquid is called *decanting*. Decanting should be done carefully to avoid clouding the supernatant liquid. Hold the rod with its lower end approximately at the level of the middle of the filter, but not touching the latter. As the filter paper fills up, raise the rod gradually together with the beaker, taking care to keep the end of the rod clear of the liquid on the filter. The level of liquid on the filter should be 3-5 mm below the edge of the paper. After filling the filter, transfer the rod carefully into the beaker, taking care not to disturb the precipitate.

Washing of precipitate. When almost all the liquid has been poured off into the filter and only the precipitate and a small amount of liquid remain at the bottom of the beaker, start washing the precipitate by decanting: wash down the particles adhering to the beaker walls with a thin jet of the wash liquid from the wash bottle. After this suspend the precipitate, stir the mixture with the rod, and allow it to settle again until the supernatant liquid is almost clear.

The accuracy of the results depends considerably on the choice of wash liquid and the amount used. If the precipitate is slightly soluble in water, it should be washed with distilled water containing a substance which yields an ion in common with the precipitate. If the precipitate is sparingly soluble in hot water, it is better to use such water for washing, because hot liquids filter more rapidly, and the solubility of impurities usually increases with increasing temperature. If the precipitate is liable to pass into the colloidal state during washing, it should be washed with water containing an electrolyte that will promote coagulation (flocculation) of the colloid. In such cases use an electrolyte which will be readily removed when the precipitate is ignited. For example, a precipitate of $MgNH_4CO_4$ should be washed with dilute ammonia solution.

The amount of wash liquid required depends on the nature of the precipitate. Jelly-like precipitates take longer to wash than crystalline ones. Finely crystalline precipitates are

much more difficult to wash than coarsely crystalline ones. The precipitate is washed much faster if the wash liquid is added in small portions. Decant each portion of the wash liquid as completely as possible from the precipitate. Washing by decantation takes less time than washing on the filter.

During filtering set the funnel with its stem clear of the filtrate. If the filtrate is needed for further analysis, collect it together with the wash waters. Otherwise discard it (if it is clear).

Test for completeness of washing. The precipitate should be washed by decanting until the liquid poured off is free from impurities. To make sure that washing may be discontinued, hold a test tube containing a small amount of a reagent that gives a characteristic reaction with the soluble substance being washed out of the precipitate under the funnel and collect a few millilitres of the filtrate in it. An alternative way of making the test is to collect 1-2 ml of the filtrate in a test tube and add a few millilitres of the reagent to it. The absence of traces of turbidity shows that the precipitate has been washed sufficiently. For example, to test for completeness of washing of a precipitate to remove soluble chlorides, pour a few millilitres each of $AgNO_3$ and HNO_3 into a test tube and hold it under the funnel to collect 1-2 ml of the filtrate. The absence of cloudiness in the test tube indicates that the washing of the precipitate is complete.

Transferring of precipitates to the filter. Transfer the thoroughly washed precipitate very carefully onto the filter through which decanting was done. For this purpose add another 20-25 ml of the wash liquid to the beaker with the precipitate and after stirring thoroughly pour the suspension formed down the rod into the funnel. Repeat this operation several times until all of the precipitate is on the filter. To wash off the traces of precipitate adhering to the beaker walls, lay the stirring rod across the beaker lip so that it extends about 3-5 cm beyond the edge. Take the beaker in the left hand and, holding the rod firmly against the beaker with the left forefinger, tilt it over the funnel so that the liquid runs down the rod into the funnel without splashing. Hold the wash bottle in your right hand and carefully wash the precipitate particles onto the filter by directing a jet

of liquid into the beaker. This will transfer almost all of the precipitate into the funnel. Keep the rod clear of the filter and of the liquid in it. The precipitate should occupy not more than one third of the filter volume, and the liquid should be 5-10 mm below the upper edge of the filter paper

Slight traces of precipitate often remain on the beaker walls and cannot be washed off with the water jet from the wash bottle. In such cases tip another glass rod with a tightly fitting ring of rubber tubing, wash it thoroughly, and rub the inside walls of the beaker with it, as well as the glass rod used initially for stirring the solution and transferring the precipitate to the filter. Collect all traces of precipitate with the rubber tip and then wash them off the latter into the funnel with a jet of water from the wash bottle. The rubber tip can be dispensed with by rubbing the residual precipitate off the beaker and rod with a piece of ash-free filter paper torn off when setting the filter in the funnel.

After filtering wash the precipitate from the top part of the filter paper into its bottom part by directing a jet of water from the wash bottle around the filter edges and spirally downwards.

Drying. To avoid contaminating the precipitate while drying, cover the funnel containing it with a sheet of filter paper (not ash-free) moistened with distilled water after writing the chemical formula of the precipitate and your name and initials on it in ordinary pencil. Tear off the paper protruding over the funnel rim, holding the paper firmly against the funnel wall with your finger. When the paper dries, it will fit snugly against the funnel edges and protect the precipitate from dust and other impurities.

Place the covered funnel with the precipitate for 20-30 min in a drying cabinet with a temperature of 90-110°C.

If the filter is not to be ignited on the same day, it need not be placed in the drying cabinet, because it will dry just as well at room temperature overnight.

125. Ignition of Precipitates

Precipitates are ignited in porcelain crucibles. They may be heated to high temperatures either in a muffle furnace or simply over a Bunsen flame. Porcelain crucibles do not

change their weight even when heated very strongly. If the substance to be ignited is liable to react with the porcelain, platinum crucibles are used instead. For instance, substances containing sodium carbonate and alkalies should not be fused in porcelain crucibles, nor should any work with fluoric acid be done in them.

Inscriptions on porcelain crucibles are made on the unglazed bottom with a solution of ferric chloride and fixed by heating the crucible strongly.

If the crucible is to be heated over a burner, it is set in a clay triangle (see Fig. 19) of sufficient size to enable the crucible to sink into it to half its height.

To clean a crucible from strongly adhering precipitates, add some concentrated nitric or hydrochloric acid and heat gently under a hood. If this does not remove the precipitate, use a mixture of three parts of nitric and one part of hydrochloric acid. If this does not clean the crucible thoroughly, it must not be used any longer for analytical work.

Preparation of crucible. Set the clean crucible in a clay triangle and calcine it with a burner for 15-20 min. The bottom of the crucible should be a few millimetres above the inner (blue) cone of the flame. Cool the calcined crucible in a desiccator to room temperature. Then weigh it, calcine it again under the same conditions for 10-15 min, cool in the desiccator, and weigh again. The permissible change in mass of the crucible after the second heating is $\pm$ 0.0004 g (otherwise the crucible should be calcined again). Such treatment is called *calcining the crucible to constant mass*..

Sometimes complete ignition of the precipitate cannot be accomplished on an ordinary gas burner; it should then be ignited in a muffle furnace or with a blowpipe after preheating with a Bunsen burner. In this case the empty crucible, prior to weighing it, is also calcined in the same manner.

The precipitate is often ignited together with the filter paper containing it. But to avoid interaction of the precipitate with the products of incomplete combustion of the filter, the precipitate should first be removed from the filter paper.

Ignition of precipitate on the filter. After calcining the crucible to constant mass, transfer the dried filter paper

with the precipitate to it as follows: set the crucible on a sheet of black glossy paper, take the filter paper by its upper edge, remove it carefully from the funnel, carry it to the crucible, fold it above the latter carefully and put it in snugly.

Sometimes traces of precipitate remain on the funnel after the filter has been removed from it. In this case wipe the funnel thoroughly with a piece of ash-free filter paper and put the latter in the crucible too. If any specks of precipitate fall on the glossy paper while transferring the filter to the crucible, shake them into the crucible as well. Then nest the crucible in a clay triangle supported on a stand ring and heat over a slow flame. When heating the crucible, take care that the filter does not burst into flame, since this may result in loss of fine particles of the precipitate. If the paper accidentally bursts into flame, do not blow at it. Remove the burner and place a lid on the crucible to prevent access of air; this will quickly extinguish the flame. Then carefully remove the lid, place the burner under the crucible again, and see that the filter continues to smoulder slowly. After smouldering stops, gradually increase the burner flame. To accelerate ignition, heat the crucible in a slanting position after the filter has burnt up, turning it from time to time with the crucible tongs. After complete combustion of the filter, continue heating for another 10-15 min.

Transfer the hot crucible to the desiccator, keep it in the weighing room until it cools down to room temperature, and weigh it. To make sure that the mass of the precipitate is constant, heat the crucible for another 10-15 min, cool in the desiccator and weigh. The difference between the two last weighings should not exceed ± 0.0004 g.

Ignition of precipitate separately from the filter. If it is necessary to remove the filter from the precipitate before ignition, shake the thoroughly dried precipitate completely onto a sheet of black glossy paper and cover it with a dry inverted funnel, closing up the end of its stem with paper or cotton wool. Carefully fold the filter paper together with the precipitate particles adhering to it above a crucible heated to constant mass and place it in the crucible. Then ignite the filter to complete combustion in the same way as when igniting the filter with the precipitate.

Combustion may result in reduction of the precipitate particles adhering to the filter and they must therefore be oxidized. For this purpose proceed as follows. After complete combustion of the filter, cool the crucible to room temperature and add 3-5 drops of concentrated HNO_3 or of 3 per cent H_2O_2 solution to its contents from a dropping bottle. Then evaporate the liquid over a slow flame carefully to avoid spattering, taking care to keep the crucible clear of the flame. When the liquid has evaporated completely and water vapours are no longer given off, heat the crucible strongly. Remove the burner, cool the crucible, set it on a sheet of glossy paper, and add the previously separated precipitate kept on another sheet of paper under the funnel to the ignited residue. Ignite the contents of the crucible again gradually increasing the flame. Cool the crucible in a desiccator, weigh it, and ignite again to constant mass.

126. Filtration Through Filtering Crucibles and Funnels

Glass and porcelain filtering crucibles with sintered glass bottoms have become popular for filtering and subsequently weighing the precipitate. Filtering funnels with similar sintered glass plates are also used. The latter are more commonly employed for preparative work, e.g., for separating crystals of a recrystallized salt from its mother liquor.

Grades and Use of Porous-Bottom Crucibles (Funnels)

Grade number	Average pore diameter, μ*	Remarks
1	100-200	For preparative work involving coarse precipitates
2	40-50	For preparative work involving fine precipitates
3	20-25	For analytical work involving amorphous precipitates, e.g., $Fe(OH)_3$, $Al(OH)_3$
4	4-10	For analytical work involving finely crystalline precipitates, e.g., $BaSO_4$

* μ stands for microns. A micron is one thousandth of a millimetre.

Depending on the pore size of the filtering plate, crucibles and funnels fall into grades denoted by the numbers 1, 2, 3, and 4 (see Table).

Filtering through porous-bottom crucibles or funnels is done under vacuum created by a water-jet or oil pump. Select the crucible or funnel of the required porosity depending on the dispersity (fineness) of the precipitate. Insert the crucible or funnel in a tightly fitting suction flask stopper (see Fig. 17). Connect the flask to a vacuum pump, switch on the latter, and pass hot distilled water through the crucible or funnel. If the crucible or funnel is a new one and has not been in use previously, first pass dilute hydrochloric acid through it under vacuum and then hot distilled water. After washing thoroughly, dry the crucible in a drying cabinet at 120-130°C for 20-30 min. Place the hot crucible in a desiccator, cool it to the temperature of the weighing room, and weigh. Then put the crucible in the drying cabinet again and dry to constant mass. Insert the dried and weighed crucible in the stopper of the suction flask, switch on the pump, and start filtering the precipitate. Decant, wash, and filter the precipitate in the same way as through filter paper. Pour the liquid to be filtered together with the precipitate into the funnel or crucible, using a rod held over the centre of the filtering plate. Take care no precipitate falls on the side walls of the crucible. During filtering do not fill the crucible to more than $^3/_4$ of its volume with liquid.

Ignite or dry the precipitate in the crucible to constant mass. Porcelain crucibles may be heated to a very high temperature in a muffle furnace; glass crucibles can only withstand a temperature of up to 600°C. Heat and cool the crucible gradually, otherwise it may crack.

After work the crucibles or funnels should be thoroughly cleaned. First shake the contents out of the crucible (funnel) and then treat it with a suitable solvent. Do not wash the crucible (funnel) with hot concentrated caustic alkali.

127. Weighing Out the Test Sample

Weigh the sample on an analytical balance to the nearest 0.2 mg (0.0002 g). First weigh a watch glass 4-6 cm in diameter and record its mass, and then place some of the

material on the glass with a spatula and weigh again (see Sec. 117). Sometimes it is more convenient to find the sample mass by the difference. Put the material to be analyzed in a weighing bottle and weigh it on an analytical balance to the nearest 0.0002 g. Take the weighing bottle out of the balance case (*hands must be clean*) and, holding it above the beaker in which the analysis is to be carried out, remove the cover from the weighing bottle with the left hand; pour some of the material into the beaker and weigh the weighing bottle again. The difference between the two weighings is the mass of the sample taken.

CHAPTER XXVIII

Calculations of Gravimetric Analysis

128. Calculation of Mass of Test Sample

A test sample is the weighed portion of material taken for the analysis. The mass of the sample depends on the percentage of the unknown component in it and on the nature of the precipitated form of the precipitate. If the precipitate is amorphous and very voluminous (as, say, $Fe(OH)_3$), a small sample may be taken for the analysis, so that the mass of the weighed form of the precipitate will be 0.10-0.15 g. If the weighed form is crystalline and the precipitate is therefore compact, the sample should be of such a mass so that the ignited precipitate weighs 0.3-0.5 g. Finally, if the precipitate is difficult to ignite, its mass should be not more than 0.1 g.

In most cases the weighed portion is from a few tenths of a gram to one gram. But if insignificant amounts of impurities (of the order of 0.001 per cent) are to be determined, a sample of several grams may be required.

Example. Suppose the percentage of barium has to be determined in a sample of crystalline barium chloride, $BaCl_2 \cdot 2H_2O$.

Calculate the mass of salt that has to be taken for the mass of the $BaSO_4$ precipitate to be approximately 0.5 g. Write the equation for the reaction:

$$BaCl_2 \cdot 2H_2O + H_2SO_4 = BaSO_4 + 2HCl + 2H_2O$$

A gram-molecule of $BaCl_2 \cdot 2H_2O$ (244.31 g) corresponds to a gram-molecule of $BaSO_4$ (233.43 g). Write the proportion:

$$\begin{gathered} 244.31 \text{ g } BaCl_2 \cdot 2H_2O \text{ yields } 233.43 \text{ g } BaSO_4 \\ x \text{ g } BaCl_2 \cdot 2H_2O \text{ yields } 0.50 \text{ g of } BaSO_4 \\ \hline x = \frac{244.31 \times 0.50}{233.43} = 0.52 \text{ g } BaCl_2 \cdot 2H_2O \end{gathered}$$

In practice the weighed portion of crystalline barium chloride may vary from 0.45 to 0.7 g.

129. Calculation of Amount of Precipitant

If the unknown can be precipitated from solution as several different compounds, choose the least soluble one. For example, Ba^{2+} ion can be precipitated as the sulphate, the chromate, the carbonate, or the oxalate. The solubility of $BaSO_4$ is 2.5 mg/lit; that of $BaCrO_4$, 2.8 mg/lit; of $BaCO_3$, 14.0 mg/lit; and of BaC_2O_4, 74.2 mg/lit. Obviously, barium is best determined as $BaSO_4$.

After selecting the precipitant, calculate the approximate amount of it (in millilitres) needed to completely precipitate the ion in question.

Example. Suppose the content of barium ions in crystalline barium chloride has to be determined. The precipitant used is sulphuric acid.

Calculate the number of millilitres of sulphuric acid needed to precipitate the barium ions.

The barium chloride sample taken for the analysis weighs 0.45 g, and a 2*N* solution of H_2SO_4 solution is used for precipitating.

According to the equation of the reaction, one mole of H_2SO_4 is required for each mole of $BaCl_2 \cdot 2H_2O$.

First calculate how many grams of H_2SO_4 are needed to precipitate Ba^{2+} from 0.45 g of $BaCl_2 \cdot 2H_2O$. Since 1 mole of $BaCl_2 \cdot 2H_2O$ weighs 244.28 g and 1 mole of H_2SO_4 weighs 98.08 g, we write the following proportion:

$$\begin{gathered} 244.28 \text{ g } BaCl_2 \cdot 2H_2O \text{ requires } 98.08 \text{ g } H_2SO_4 \\ 0.45 \text{ g } BaCl_2 \cdot 2H_2O \text{ requires } x \text{ g } H_2SO_4 \\ \hline x = \frac{98.08 \times 0.45}{244.28} = 0.1803 \text{ g of anhydrous } H_2SO_4 \end{gathered}$$

Then calculate how many millilitres of $2N$ H_2SO_4 solution are required to precipitate all the barium as sulphate:

1000 ml of $2N$ solution contain 98 g H_2SO_4
x ml of $2N$ solution contain 0.18 g H_2SO_4

$$x = \frac{0.18 \times 1000}{98} \approx 2 \text{ ml of } 2N \text{ } H_2SO_4$$

Practically 4 or 5 ml of $2N$ H_2SO_4 solution should be taken, because the precipitant should be added in excess. Usually a 50 to 100 per cent excess of precipitant is added over and above the amount calculated.

130. Calculation of the Percentage of an Unknown in the Test Sample

In gravimetric analysis the unknown component is isolated as an insoluble compound (precipitate). After drying or igniting, the composition of the precipitate corresponds to a definite chemical formula.

Since it is usually required to calculate the percentage of the unknown in the sample, it is necessary to know the sample mass and the mass and chemical formula of the resulting precipitate (weighed form)[1].

Example 1. A portion of limestone weighing 0.5015 g, was found by analysis to contain 0.3248 g of CaO. Determine the percentage of calcium oxide and of calcium in the limestone sample.

Solution. Write the following proportion:

0.5015 g of limestone contains 0.3248 g CaO
100 g of limestone contain x g CaO

$$x = \frac{0.3248 \times 100}{0.5015} = 64.77\% \text{ CaO}$$

To calculate the percentage of calcium, first determine the amount of calcium contained in the precipitate produced (0.3248 g of CaO). The molecular mass of CaO is 56.08, and the atomic mass of Ca is 40.08. Write the following propor-

[1] The chemical formula of the material under analysis is not necessarily known.

tion

$$\begin{array}{l} 56.08 \text{ g CaO contain } 40.08 \text{ g Ca} \\ 0.3248 \text{ g CaO contains } x \text{ g Ca} \end{array}$$

$$x = \frac{0.3248 \times 40.08}{56.08} = 0.2321 \text{ g Ca}$$

By calculating the amount of the unknown in the precipitate we have also found the amount of it contained in the weighed portion. For instance, if there is 0.2321 g of Ca in the precipitate the amount of calcium in the weighed portion (0.5015 g) will be the same. Determine the percentage of calcium in the material analyzed from the following proportion:

$$\begin{array}{l} 0.5015 \text{ g of limestone contains } 0.2321 \text{ g Ca} \\ 100 \text{ g of limestone contain } x \text{ g Ca} \end{array}$$

$$x = \frac{0.2321 \times 100}{0.5015} = 46.28\% \text{ Ca}$$

Example 2. When analyzing 0.8105 g of an alloy the precipitate of Al_2O_3 obtained weighed 0.5008 g. Determine the percentage of aluminium in the alloy.

Calculate the amount of aluminium in the precipitate. The molecular mass of aluminium oxide Al_2O_3 is 101.96; the atomic mass of aluminium is 26.98. Since 1 mole of Al_2O_3 contains 2 g-atoms of Al, write the following proportion:

$$\begin{array}{l} 101.96 \text{ g } Al_2O_3 \text{ contain } 2 \times 26.98 \text{ g Al} \\ 0.5008 \text{ g } Al_2O_3 \text{ contains } x \text{ g Al} \end{array}$$

$$x = \frac{2 \times 26.98 \times 0.5008}{101.96} = 0.2650 \text{ g Al}$$

Calculate the percentage of aluminium in the alloy. The amount of aluminium found is the amount of it contained in the weighed portion. Hence,

$$\begin{array}{l} 0.8105 \text{ g of the alloy contains } 0.2650 \text{ g Al} \\ 100 \text{ g of the alloy contain } x \text{ g Al} \end{array}$$

$$x = \frac{0.2650 \times 100}{0.8105} = 32.69\% \text{ Al}$$

Thus, to calculate the content of the component to be determined in the precipitate, multiply the mass of the dried or ignited precipitate by the molecular or atomic

mass of the unknown and divide the product by the molecular mass of the compound in the precipitate.

Use the following formula for calculations in gravimetric analysis:

$$P = \frac{b \cdot 100}{B} \%$$

where P = percentage of unknown;
b = mass of unknown in the precipitate;
B = weighed portion.

If the weighed form and the unknown are one and the same, substitute the amount of the weighed form obtained for b in the above equation. For instance, to determine the content of CaO in limestone use the formula

$$P = \frac{\text{mass of precipitate} \times 100}{\text{weighed portion}} \%$$

Very often the chemical composition of the unknown differs from the composition of the precipitate obtained, though the unknown is always a component of the precipitate. For example, when determining the content of iron (metallic iron Fe) it is weighed as Fe_2O_3.

In such cases first calculate the amount of the unknown in the precipitate obtained:

$$b = \frac{B \cdot A}{M}$$

where b = mass of unknown in precipitate;
B = mass of precipitate;
A = atomic or molecular mass of unknown;
M = molecular mass of unknown in precipitate.

The ratio A/M is called the *conversion*, *analytical*, or *gravimetric factor* (F). It shows how many grams of the unknown are contained in 1 g of the precipitate. When determining the content of calcium by weighing it as CaO the conversion factor is

$$F_{\text{Ca/CaO}} = \frac{A_{\text{Ca}}}{M_{\text{CaO}}} = \frac{40.08}{56.08} = 0.7147$$

The conversion factor equals the ratio of equivalent amounts of the unknown and the substance weighed. Hence,

in the ratio for the conversion factor the atomic or molecular mass of the unknown is in the numerator and the molecular mass of the weighed component (precipitate) is in the denominator. When calculating the conversion factor, the numerator and denominator should contain equal numbers of the atoms of the unknown.

For instance, when calculating the mass of aluminium from the mass of ignited aluminium oxide, the chemical factor is

$$F_{Al/Al_2O_3} = \frac{2Al}{Al_2O_3} = 0.5293$$

CHAPTER XXIX

Examples of Gravimetric Analysis

131. Quantitative Determination of Hydrated Water in Crystalline Barium Chloride

Solids may contain hygroscopic water and/or water of crystallization. The amount of hygroscopic water in a substance varies widely depending on how finely it is divided and on the humidity of the ambient atmosphere; it is found by means of the moisture content determination described in Sec. 132.

Substances containing water of crystallization are called *crystalline hydrates.*

The amount of crystallization water in a crystalline hydrate is strictly definite for each substance. Some crystalline hydrates may lose part of their crystallization water if stored in dry air. This process is called *efflorescence* of crystals. On the other hand, other crystalline hydrates take up moisture from moist air. This phenomenon is called *deliquescence* of crystals.

To keep crystalline hydrates from changing their composition (i.e., from deliquescing or effloresc ing), they are st ored in jars with ground-glass stoppers.

To determine the amount of crystallization water in a crystalline hydrate, first consult a handbook to find out the temperature at which the substance loses its water of crystallization, and then remove it at that temperature. For

instance, the content of crystallization water in $BaCl_2 \cdot 2H_2O$ should be determined at 120-125°C.

Procedure. 1. Wash a weighing bottle thoroughly, wipe it dry on the outside with a towel and dry it with its cover inserted on edge in a drying cabinet for 30 to 40 min at 120-125°C. Cool the weighing bottle and its cover in a desiccator in the weighing room (this usually requires 15-20 min).

Weigh the weighing bottle with its cover on an analytical balance and record the result in the laboratory notebook. After the first weighing, put the weighing bottle back in the drying cabinet and keep it there at the same temperature as before for 20 or 30 min. After cooling in the desiccator weigh it again and write down the result. If the mass of the weighing bottle has not changed or has changed insignificantly (not more than 0.0004 g), drying may be considered complete.

2. Put 2-3 g of crystalline barium chloride in the dried and weighed weighing bottle, weigh it, and record the mass of the weighing bottle with the substance in your notebook.

3. Open the weighing bottle and dry it together with its cover during 1.5-2 hours in the drying cabinet. The temperature in the drying cabinet throughout this period should be 120-125°C. At a higher temperature, $BaCl_2$ will decompose; at a lower one, not all the water of crystallization will come off.

4. Cover the weighing bottle, cool in the desiccator and weigh. Dry again under the same conditions for half an hour and, after cooling in the desiccator, reweigh the weighing bottle with the substance and repeat dryings and weighings until the mass of the weighing bottle with the $BaCl_2$ remains constant (the difference between two weighings does not exceed 0.0004 g).

A model record of the results is shown below.

Date
Name of analysis

Weighing barium chloride before drying

Mass of weighing bottle after first drying	24.3240 g
Mass of weighing bottle after second drying	24.3238 g
Final mass of weighing bottle	24.3238 g
Mass of weighing bottle with initial sample	27.0141 g
Mass of barium chloride	2.6903 g

Weighing barium chloride after drying

Mass of weighing bottle with sample after first drying	26.6172 g
Mass of weighing bottle with sample after second drying	26.6165 g
Mass of weighing bottle with sample after third drying	26.6161 g
Final mass of weighing bottle with barium chloride	26.6161 g

Calculation

Mass of crystallization water:

$$27.0141 - 26.6161 = 0.3980 \text{ g}$$

Percentage of crystallization water:

2.6903 g of the sample contain 0.3980 g H_2O
100 g of the sample contain x g H_2O

$$x = \frac{0.3980 \times 100}{2.6903} = 14.79\% \text{ of water}$$

Compare the result obtained with the theoretical content of crystallization water calculated from the chemical formula:

Molecular mass of $BaCl_2 \cdot 2H_2O$ . . . 244.28
Molecular mass of H_2O 18.016

244.28 g of C.P. $BaCl_2 \cdot 2H_2O$ contain 36.03 g H_2O
100 g of C.P. $BaCl_2 \cdot 2H_2O$ contain x g H_2O

$$x = \frac{36.03 \times 100}{244.28} = 14.75\%$$

The error of the determination can be found by comparing the result of the analysis with the amount of water in $BaCl_2 \cdot 2H_2O$ calculated theoretically:

$$14.79 - 14.75 = 0.04\%$$

The relative error in per cent can be calculated from the following proportion:

$$14.75 - 0.04$$
$$100 - x$$

$$x = \frac{0.04 \times 100}{14.75} = 0.27\%$$

132. Determination of Moisture Content

Moisture content is determined in the same way as water of crystallization, but at a different drying temperature (mostly at 105-110°C). Since the sample should have as large a surface area as possible, it is first ground to a powder (minerals, coal, salts, etc.) or cut up into small pieces (paper, leather, etc.).

Dry the weighing bottle with its cover in a drying cabinet at 105-110°C to constant mass and cool in a desiccator in the weighing room. Place 2 to 5 g of an average sample of the material (the weighed portion) in the weighed weighing bottle. Put the weighing bottle with the weighed portion in the drying cabinet and dry it to constant mass at 105-110°C. The loss in mass equals the amount of moisture contained in the weighed portion. Moisture content is expressed in per cent of the weighed portion.

133. Determination of Ash Content

Organic compounds usually contain various inorganic impurities which remain as ash when the organic matter is burnt. When determining the ash content, combustion must be complete, i.e., only mineral matter should remain in the ash; all the organic matter should be burnt out and all the volatile components should be removed.

Ashing is carried out as follows:

1. Calcine a crucible with its cover to constant mass (see Sec. 125).
2. Weigh out 1-2 g of the unknown substance into the crucible.
3. Place the covered crucible in a clay triangle on a ring and heat it gently at first, keeping the crucible bottom clear of the flame. This will result in the dry distillation of the substance: gases will be evolved and the inside of the crucible and its cover will be coated with a brownish black tarry deposit. Take care that the dry distillation products do not deposit on the outside surface of the crucible walls. This may occur if a strong flame is applied right away. After vapours and gases have stopped evolving, open the crucible cover a little and increase the flame gradually, bringing it closer to the crucible.

To facilitate access of air, place the crucible in an inclined position, turning its smoked walls towards the flame from time to time.

Sometimes complete ashing of the substance cannot be accomplished for a very long time. In such cases cool the crucible, moisten the residue with 1-2 ml of 3 per cent hydrogen peroxide solution. Allow the added solution to soak in thoroughly. Add another millilitre of hydrogen peroxide, evaporate carefully to dryness, and then gradually increase the flame and calcine to complete ashing, i.e., until the incombustible residue is completely free from carbon and the ash becomes absolutely white.

4. Cool the crucible in a desiccator and weigh. Calculate the ash content from the difference between the mass of the crucible with the ash and that of the empty crucible.

Model Calculation

Weighed portion	1.2025 g
Mass of crucible with ash	12.5842 g
Mass of crucible without ash	12.5220 g
Mass of ash	0.0622 g

Percentage of ash:

$$\frac{0.0622 \times 100}{1.2025} = 5.17\%$$

134. Quantitative Determination of Barium in Crystalline Barium Chloride

Barium is determined quantitatively by precipitating it as barium sulphate, $BaSO_4$, the SO_4^{2-} ions needed for precipitating the Ba^{2+} ions being added as H_2SO_4:

$$Ba^{2+} + SO_4^{2-} = BaSO_4$$

Precipitation. Weigh a watch glass on an analytical balance to the nearest 0.0002 g. On this watch glass weigh out a 0.5-0.7 g portion of crystalline barium chloride with the same accuracy. Transfer the weighed portion carefully to a clean 200-300 ml beaker; hold the watch glass inclined over the beaker and wash the glass thoroughly with a jet of water from a wash bottle, taking care that all of the liquid drips into the beaker. Dilute the resulting solution with

water to 75-100 ml, stirring it with a glass rod. If the stirring rod has a rubber tip on it, stir with the opposite untipped end.[1] Do not remove the rod from the beaker until precipitation is complete, because drops of the solution remain on it and this will affect the accuracy of the analysis result. Add 2-3 ml of 2*N* HCl solution and heat it almost to boiling[2], but do not boil because the evolving vapour may entrain droplets of liquid from the beaker.

To another small beaker add 5-6 ml of 2*N* H_2SO_4 solution (calculate the amount of precipitant needed as described in Sec. 129). Dilute with water to 40-50 ml and heat to boiling. Add hot H_2SO_4 to the hot barium chloride solution slowly, drop by drop, stirring constantly with a glass rod. At the beginning of precipitation add the H_2SO_4 slowly, and the last 3-5 ml faster.

Place the beaker with the precipitate immediately in a boiling water bath and allow the suspension to settle. Precipitation with heating and slow cooling in a hot bath promotes the formation of a coarser precipitate. When the supernatant liquid becomes clear, check for completeness of precipitation as follows: carefully add 2 or 3 drops of H_2SO_4 (it may be cold) to the solution down the beaker walls. If no cloudiness forms at the point of incidence of the acid drops (a slight disturbance of the precipitate at the bottom of the beaker is permissible), precipitation is considered complete. Cover the beaker with a piece of moist filter paper, piercing it with the stirring rod, and allow it to stand for 2-3 hours or (which is better) overnight.

Washing and filtering of precipitate. Use close-texture (blue band) filter paper. Fit it snugly in the funnel and decant the clear supernatant liquid through the filter. To do so, carefully pour the liquid off the precipitate down the stirring rod held firmly against the beaker lip, without disturbing the precipitate. Between consecutive fillings of the filter, keep the stirring rod in the beaker, but do not

[1] If you happen to lower the tip by accident into the solution, remove the rod from the solution, rinse it thoroughly with distilled water above the beaker with the solution to be analyzed and stir the latter with a clean untipped rod.

[2] Hydrochloric acid is added to prevent the formation of a colloidal solution and to ensure formation of larger $BaSO_4$ crystals.

allow it to touch the inside of its lip; remove and replace it in the solution without disturbing the precipitate.

Wash the precipitate several times with cold water by decantation. After 4 or 5 decantations check for completeness of removal of SO_4^{2-} ions as follows. Collect the last 1-2 ml of filtrate running out of the funnel, add 1-2 ml of 2*N* HNO_3 and 3 or 4 drops of 0.5*N* $BaCl_2$ solution. No turbidity should appear in the test tube; if it does appear, continue washing. After removing the SO_4^{2-} ions from the precipitate, transfer the latter carefully onto the filter. Cover the funnel with a moist piece of filter paper and dry the precipitate in a drying cabinet at 100-110°C (see Sec. 124).

Ignition of precipitate. Calcine a crucible to constant mass. Transfer the filter paper with the precipitate carefully to the crucible and ignite on a slow burner flame. After complete carbonization of the filter, increase the burner flame and continue heating the crucible with the precipitate to complete disappearance of traces of carbon on the crucible walls and in the precipitate.

Cool the crucible in the desiccator, weigh and ignite to constant mass; for this purpose it is usually sufficient to reignite only once.

A model record of experimental results is given below.

Date
Name of analysis

Weighing crystalline barium chloride

Mass of watch glass with barium chloride . . . . . .
Mass of watch glass . . . . . .
Mass of barium chloride . . . . . .

Weighing barium sulphate, $BaSO_4$

Mass of crucible after first calcination . . . . . .
Mass of crucible after second calcination . . . . . .
Mass of crucible with $BaSO_4$ after first ignition . . . . . .
Mass of crucible with $BaSO_4$ after second ignition . . . . . .
Mass of $BaSO_4$ . . . . . .

Calculation

If 0.5850 g of barium chloride was taken for the analysis and the mass of $BaSO_4$ precipitate found to be 0.5642 g, determine how much barium is contained in the amount of $BaSO_4$ obtained.

As the molecular mass of $BaSO_4$ is 233.43 and the atomic mass of barium is 137.36, write the following proportion:

$$\begin{array}{l} 233.40 \text{ g } BaSO_4 \text{ contain } 137.34 \text{ g Ba} \\ 0.5642 \text{ g } BaSO_4 \text{ contains } \quad x \text{ g Ba} \end{array}$$

$$x = \frac{137.34 \times 0.5642}{233.40} = 0.3319 \text{ g Ba}$$

This is the amount of barium contained in the weighed portion of the barium chloride sample.

The content of barium in $BaSO_4$ can also be calculated by using the analytical or conversion factor (see end of Sec. 130) equal to

$$F_{Ba/BaSO_4} = \frac{137.34}{233.40} = 0.5884$$

Substituting this value into the equation, find the value of x:

$$x = 0.5884 \times 0.5642 = 0.3319 \text{ g}$$

The percentage of barium in the weighed sample is found from the following proportion:

$$\begin{array}{l} 0.5850 \text{ g of the sample contains } 0.3319 \text{ g Ba} \\ 100 \text{ g of the sample contain } \quad x \text{ g Ba} \end{array}$$

$$x = \frac{0.3319 \times 100}{0.5850} = 56.74\%$$

To compare the result obtained with the content of barium in chemically pure $BaCl_2 \cdot 2H_2O$, calculate the percentage of barium in $BaCl_2 \cdot 2H_2O$:

$$\begin{array}{l} 244.28 \text{ g } BaCl_2 \cdot 2H_2O \text{ contain } 137.34 \text{ g Ba} \\ 100 \text{ g } BaCl_2 \cdot 2H_2O \text{ contain } \quad x \text{ g Ba} \end{array}$$

$$x = \frac{137.34 \times 100}{244.28} = 56.22\%$$

If the salt taken for the analysis was chemically pure, the error of the analysis is:

$$56.74 - 56.22 = 0.52\%$$

The relative error in per cent is calculated from the following proportion:

$$\begin{array}{l} 56.22 - 0.52 \\ 100 - x \end{array}$$

$$x = \frac{0.52 \cdot 100}{56.22} = 0.92\%$$

135. Quantitative Determination of Iron in Ferric-Ammonium Alum

Fe^{3+} ion is precipitated with ammonium hydroxide as amorphous $Fe(OH)_3$.

Precipitation. Weigh out approximately 0.7-0.8 g of the alum to the nearest 0.0002 g on an analytical balance into a 200-300 ml beaker, add 5-10 ml of 2*N* H_2SO_4 solution, 50-100 ml of hot water, add 5-8 drops of concentrated HNO_3 (to oxidize Fe^{2+} to Fe^{3+}). Heat the beaker carefully on a slow burner flame for 3-5 min without allowing the liquid to boil. Remove the beaker from the asbestos gauze and add 10 per cent ammonia solution slowly, drop by drop, to the hot solution, stirring constantly.

If the iron has not been pre-oxidized sufficiently, the precipitate will be black or greenish-black (mixture of oxides and hydroxides of Fe^{2+} and Fe^{3+}) instead of reddish-brown. In this case stop adding NH_4OH and redissolve the precipitate formed by adding concentrated HCl (avoid a large excess of HCl). Add about 1 ml of concentrated HNO_3 or 3 per cent hydrogen peroxide solution. Heat the solution again to boiling and reprecipitate the iron with ammonia solution. Add ammonia until the solution under test acquires the odour of NH_3. If no odour of ammonia is noticeable after stirring the mixture thoroughly, add a few more drops of NH_4OH. After a red-brown precipitate of $Fe(OH)_3$ is formed, add 80-90 ml of hot water to the beaker and heat the mixture again, stirring constantly, almost to boiling. Allow the precipitate to settle in a boiling water bath for 3-5 minutes.

Filtration. Prepare a wash bottle with a hot 2 per cent NH_4NO_3 solution, a beaker (flask), and a funnel with a snugly fitting filter of medium texture (white band). Decant, i.e., pour off the hot clear solution down a glass rod onto the filter without disturbing the precipitate. Add 10-15 ml of hot water to the precipitate, stir the mixture, allow it to settle for a short time and pour the clear solution off onto the filter. Add water in small portions (10-15 ml), taking care to transfer as little of the precipitate as possible to the filter. After four or five decantations[1] check for completeness of

[1] If hydrochloric acid was added during the analysis or ferric chloride was taken for the analysis.

removal of SO_4^{2-} or Cl^- ions from the precipitate. Wash waters should not give a precipitate in the presence of HNO_3 with either $AgNO_3$ or $BaCl_2$; if turbidity appears, continue washing the precipitate (the precipitate cannot be left on the filter overnight unless it is completely washed). Transfer the thoroughly washed precipitate to the filter, washing it carefully off the beaker bottom and walls with a strong jet of water. If the last traces of precipitate do not wash off with the water jet and cannot be removed with the rubber tip, wipe the inside walls of the beaker and the stirring rod with a small piece of ash-free filter paper and put it in the filter with the precipitate. The entire process of precipitating, washing, and filtering the precipitate must be completed in the course of one lesson.

Ignition of the precipitate. Cover the funnel containing the precipitate with a piece of filter paper moistened with distilled water and keep it in a drying cabinet for 1 hour at 100-110°C (if the precipitate is to be left standing overnight do not put it in the drying cabinet). Remove the dried filter with the precipitate from the funnel, fold it, put it in a weighed crucible, and heat it over a gas burner. Place the crucible in an inclined position in a clay triangle and heat the bottom of the crucible with the upper oxidizing part of the flame. After the filter has burned up set the crucible vertically and heat strongly for 30-40 minutes (do not use a muffle furnace). Transfer the crucible to a desiccator and after it has cooled down, weigh it. Ignite the crucible with the precipitate to constant mass. Knowing the mass of Fe_2O_3, calculate the percentage of iron in the sample.

Example. Suppose a g of the alum was taken for analysis and b g of Fe_2O_3 was obtained. Calculate how many grams of iron is contained in the resulting Fe_2O_3 precipitate.

As the molecular mass of Fe_2O_3 is 159.7, and the atomic mass of iron is 55.85, write the following proportion:

$$\begin{array}{r} Fe_2O_3 \text{ g contains } 2Fe \text{ g} \\ \hline b \text{ g contains } \quad x \text{ g} \end{array}$$

$$x = \frac{2Fe \cdot b}{Fe_2O_3}$$

and calculate the analytical factor:

$$\frac{2Fe}{Fe_2O_3} = 0.6994$$

Hence, $x = b \cdot 0.6994$.

The percentage of iron in the sample is

$$\frac{b \cdot 0.6994 \cdot 100}{a} \%$$

Questions and Problems

1. How much precipitant (equivalent or excess amount) is used in gravimetric analysis to precipitate the desired ion more completely?
2. Does the exact concentration of the precipitant have to be known in gravimetric analysis?
3. What are the precipitated and weighed forms of the precipitate?
4. What are the requirements for the precipitated and the weighed form?
5. Why are precipitates sometimes washed with a dilute solution of a salt containing an ion in common with the precipitate, rather than with pure water?
6. In what cases are filters burned and ignited together with the precipitate and in what cases are they treated separately?
7. How is the moisture content in a sample determined?
8. State and explain the conditions of precipitating Ba^{2+} ions from solutions of its salts.
9. Why is NH_4OH used as the precipitant rather than KOH or NaOH when Fe^{3+} ions are precipitated as $Fe(OH)_3$?
10. What is the *analytical* or *conversion factor*?
11. Determine the percentage of moisture in a sample from the following data: mass of weighing bottle = 8.1748 g; mass of weighing bottle with weighed portion before drying = 11.8245 g; mass of weighing bottle with weighed portion after drying = 11.3248 g.

Ans. 13.69%

12. How many millilitres of a barium chloride solution containing 30 g of $BaCl_2 \cdot 2H_2O$ in one litre is needed to precipitate the SO_4^{2-} ions from a solution containing 0.5 g of potassium sulphate?

Ans. 23.36 ml

13. Suppose 0.3000 g of $Mg_2P_2O_7$ was obtained from 0.9580 g of commercial magnesium sulphate (heptahydrate). Determine the percentage of magnesium in the sample under test.

Ans. 6.84%

14. Calculate the volume of 0.1*N* $AgNO_3$ solution required to precipitate Cl^- from a solution containing 0.2923 g of sodium chloride.

Ans. 50.0 ml

15. How many millilitres of HCl (sp gr 1.13) are required to dissolve 0.5 g of $CaCO_3$?

Ans. 1.24 ml

16. On analyzing 0.9000 g of magnesite, it was found to contain: 0.0420 g of Fe_2O_3, 0.0582 g of CaO, and 1.4920 g of $Mg_2P_2O_7$. Calculate the percentage of ferric oxide, iron, calcium oxide, calcium, magnesium oxide, and magnesium in the sample.

Ans. 4.67% Fe_2O_3; 3.26% Fe; 6.47% CaO; 4.62% Ca; 60.06% MgO; 36.23% Mg

VOLUMETRIC ANALYSIS

CHAPTER XXX

Introduction to Titrimetric Analysis

136. General Principles

In gravimetric analysis the desired constituent of the dissolved sample under test is converted to an insoluble compound of known composition and the amount of the constituent is calculated from the mass of the compound precipitated. Volumetric analysis is based on the measurement of two reacting solutions, one of which contains the substance under test and the second is of exactly known concentration. The concentration of the constituent sought is determined from the stoichiometric (equivalent) quantities of reagent and constituent that react and the known concentration of one of the solutions. The process of measurement of volume is called *titration* and the method of analysis involving titration is termed *titrimetric analysis.*[1] The solution of known concentration used to determine the amount of the sought constituent is called the *titrant* (or *standard solution*).

For instance, it is necessary to determine the percentage of chloride in sodium chloride. This can be done in two ways: by gravimetric or titrimetric analysis.

In gravimetric analysis a weighed portion of the substance under test is dissolved in water and the chloride ion is precipitated quantitatively as AgCl. The precipitant (dilute $AgNO_3$ solution) is added in excess. The concentration of silver nitrate solution may be unknown. The amount of

[1] The measurement of a gas volume also constitutes a volumetric analysis; accordingly, the less ambiguous term *titrimetric analysis* is preferred to volumetric analysis.

chloride is found by calculation after determining the mass of the precipitate of AgCl.

In titrimetric determination of chloride in sodium chloride, it is necessary to use an $AgNO_3$ solution of known concentration and to determine the exact volume of silver nitrate that is equivalent to the analyzed quantity of sodium chloride. The equivalent volume is determined by titrating the NaCl solution with the $AgNO_3$ solution.

In titrimetric analysis, the following conditions must be fulfilled:

1. The reaction between the reagent and substance under test must go to an end and do so quickly and quantitatively.
2. The moment when the stoichiometric (equivalence) point of the reaction has been reached (the reaction is completed) must be indicated visibly by a change in colour of the solution or the appearance of a coloured precipitate. Most titrations involve the use of certain substances known as *indicators* whose function is to clearly indicate the *end-point* of titration (i.e., the moment when the colour change occurs).
3. The concentration of one of the solutions (the titrant) must be known.
4. Other substances that may be present in the solution must not interfere with the basic reaction.

Review Questions

1. On what is the gravimetric method of analysis based?
2. On what is the titrimetric method of analysis based?
3. What conditions must be fulfilled for conducting titrimetric analysis?

137. Titration Methods

According to the type of reaction that takes place in the given titration, there are several methods of titrimetric analysis. The methods most commonly used are:

(1) acid-base titrations (acidimetry and alkalimetry);

(2) oxidation-reduction titrations (oxidimetric and reductimetric titrations), including the permanganate and iodometric methods;

(3) precipitation titrations, including argentimetry (Mohr's method) and titrations with thiocyanate (Volhard's method);

(4) complexometric (chelatometric) titrations.

138. Titration Procedure

The purpose of titration is to measure the volume of two solutions containing equivalent quantities of the reacting substances.

Titration involves the determination of the end-point of the reaction, i.e., the moment when the volume of the solution of exactly known concentration (titrant) added contains a quantity of substance equivalent to the amount of the substance being determined. This moment is called the *stoichiometric point* or *equivalence point.*

Titration is carried out as follows. Fill the burette with the titrant to the zero mark, taking care that there are no air bubbles at the bottom. Measure off the solution under test with a pipette and transfer it to a conical flask. Then add a few drops of a suitable indicator (unless one of the solutions is itself an indicator). To the solution in the flask gradually add the solution from the burette until the colour of the solution in the flask changes. At the beginning, the solution from the burette should be added in a thin stream, constantly mixing the contents of the flask by swirling. Towards the end-point, the titrant should be added more slowly and, finally, drop by drop.

During the titration, the stopcock (or clip) of the burette should be held in the left hand. The flask containing the liquid being titrated is held in the right hand and should be continually swirled to mix the solution contained in it.

The results of titration will be correct if at the end-point the colour of the solution being titrated changes sharply on adding a single drop of the titrant. In order to view the change in colour more easily, the flask with the solution being titrated is placed on a white tile or a glass plate covering a sheet of white paper. Besides that, a reference solution should be prepared and the test solution titrated to the same colour. For this purpose take 40-50 ml of distilled water, add a single drop of the standard solution and

the same amount of indicator as was added to the titrated solution. Compare the colour of the reference solution with that of the titrated solution. Finally, the end-point of titration can be checked by adding a drop of the solution under analysis to the titrated solution; the colour of the solution should change sharply.

The result of the first titration is usually not very exact and therefore only approximate. It is recommended that in the first titration 1 ml of the titrant be added at a time from the burette in order to find the limits within which the equivalence point lies. For instance, if the addition of 23 ml of the titrant causes no change in colour and the addition of 24 ml results in a sharp change in the colour of the solution, the equivalence point lies between 23 and 24 ml.

In the second titration, 23 ml of the titrant are added quickly to the solution under test, constantly mixing the contents of the flask, and then the titrant is added drop by drop until the colour of the indicator changes.

The volume of the titrant used in each titration is measured by the graduation marks on the burette and reported in the laboratory notebook. Each solution is carefully titrated at least three times. The results of titration should differ from each other by not more than 0.05 ml. The concentration of the solution is calculated from the arithmetical mean volume.

There are three methods of titration: direct titration, back titration, and displacement titration.

In *direct titration* the solution under test is directly titrated with a standard solution: for example, titration of hydrochloric acid with sodium hydroxide, reducing agents with potassium permanganate, sodium chloride with silver nitrate solution.

Back titration is used when the substance under analysis does not react with a given standard solution or reacts with it very slowly. In this case, to the solution under test is added a definite amount of a third substance (capable of reacting with the substance under test) which is taken in excess, and the excess of the third substance is titrated with the standard solution. The concentration of the third (additional) solution is determined by previously titrating it with the standard solution. An example of back titration

is the determination of oxidizing agents by back titration with potassium permanganate (see Sec. 164).

Displacement titration is used in those cases when the ion being determined: (a) does not react directly with the standard solution; (b) does not react with the standard solution stoichiometrically; (c) does not interact with the indicator. The ion to be determined is first converted to some other chemical compound which can be titrated directly with the standard solution. An example of such a titration is the determination of oxidizing agents by iodometric analysis (see Sec. 170).

139. Indicators

Indicators are substances that are used to indicate visibly the moment when the equivalence point has been reached between the solutions in a titration.

Generally, indicators are substances that give a colour reaction with one of the reacting substances. For example, starch reacts with iodine solution to give an intense blue colour. Hence, starch is an indicator of free iodine. One and the same indicator is coloured differently in different conditions. Phenolphthalein for example is colourless in acidic and neutral solutions but turns red-violet in alkaline solutions.

Sometimes one of the reacting substances serves as its own indicator. An example is when a reducing agent is added slowly to an acidic solution of the oxidizing agent $KMnO_4$, the solution is decolourized at once. On adding a single excess drop of $KMnO_4$, the solution assumes a pale pink colour.

CHAPTER XXXI

Apparatus Used in Titrimetric Analysis

140. Volumetric Glassware

The apparatus required in titrimetric analysis for the accurate measurement of volume includes graduated flasks, pipettes, and burettes.

Graduated flasks are used to prepare solutions and to measure off a fixed volume of a liquid. The flasks are thin-walled, flat-bottomed vessels with a long cylindrical neck round which the graduation mark extends (Fig. 27). Each flask bears, in addition, a mark indicating its volume and the temperature at which the volume was measured. The flask should be tightly stoppered. Those with ground-glass stoppers are the most convenient for mixing. Graduated flasks are available in sizes ranging from 5 ml to 5 litres; the most commonly used capacities are 1000, 500, 250, 200, and 100 ml.

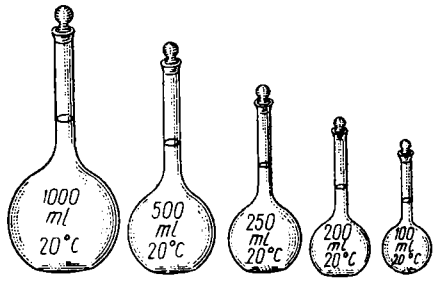


Fig. 27. Graduated flasks

The graduated flask is filled with liquid until its lower meniscus touches the graduation mark; the observer's eyes should be at the same level as the mark on the flask.

On no account must graduated flasks be heated, because this might change their capacity (cubic content).

If heating is required to achieve complete dissolving of the sample under test, the latter must be previously heated in another vessel. To prepare a solution, carefully transfer the weighed portion of the sample to a flask through a funnel, taking care that there are no losses. When all the material has been transferred to the flask, add water so that approximately half of the flask is filled. Mix the contents of the flask thoroughly with a swirling motion until the material is completely dissolved. Then add water to a level 3-5 ml below the graduation mark and make up to the mark with water, adding it drop by drop. Stopper the flask and mix

thoroughly to attain the same concentration of the solution throughout the entire volume.

Pipettes are used to deliver a fixed volume of a liquid sample. There are two general types of pipette. The ordinary (transfer) pipette (Fig. 28*a*) is a glass tube with a bulb in the middle and with a capillary (tapered) tip at the bottom; at the top it has a graduation mark that indicates to what

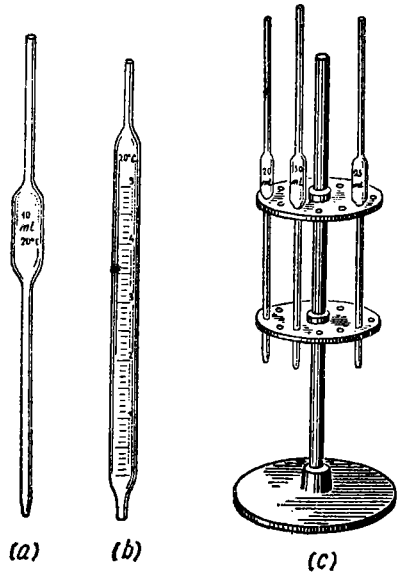


Fig. 28. Pipettes
a — transfer; b — measuring; c — pipette holder

height it should be filled with the liquid being measured. The pipette also bears a mark indicating its capacity and the temperature at which the capacity was measured. The usual capacities are 10, 20, 25, and 50 ml.

The measuring pipette (Fig. 28*b*) is used to measure variable volumes of liquid. It is a glass tube with a tapered end and a series of graduation marks indicating the volume in parts of a millilitre.

Prior to use, the pipette must be thoroughly washed as follows. Connect a looped glass tube to the top of the pipette

by means of a short rubber tube provided with a metal pinch clip and carefully suck in dichromate-sulphuric acid cleaning mixture from a tall cylinder[1]. Great care should be taken when working with the cleaning mixture, because it can cause bad burns. If the pipette does not become adequately clean at once, it should be filled with the mixture and allowed to stand for 1-2 hours (or even overnight). Then drain the pipette and wash it with a jet of tap water. The inside of the pipette should be uniformly wetted with water so that drops do not remain on it.

Just before use, rinse the pipette with distilled water and then with the solution with which it will be filled. To fill the pipette, dip the tapered tip into the liquid and suck the latter in with the mouth from the other end, just above the graduation mark. To avoid frothing and air bubbles, dip the pipette deep enough into the solution, suck in the liquid above the mark, and quickly close the top of the pipette with the forefinger of the right hand. Withdraw the pipette from the liquid. Holding it in a vertical position, wipe the outside of the pipette dry and by gentle release of the pressure allow the liquid to fall to the mark, a drop at a time, until the lower part of the concave meniscus touches the mark. Hold the discharge tip of the pipette against the inside of a conical titration flask, lift the forefinger and allow the liquid to drain freely from the pipette. To remove liquid remaining in the tip of the pipette, hold it against the wall of the vessel for another 15 seconds. The last drops of liquid should not be blown or shaken out.

Burettes (Fig. 29) are used to determine the equivalent volumes of two reacting solutions, i.e., for titrating (see Sec. 138).

A burette is a long glass tube of uniform bore throughout the length, graduated in tenths of a millilitre. The most commonly used sizes are 25- and 50-ml burettes. The burette is usually closed at the bottom by a glass stopcock or it has a small bulb at the end on which is fitted a rubber tube with a pinch clip and a capillary tip. Sometimes instead of a clip, a glass ball of a diameter slightly larger than the inside dia-

[1] The dichromate-sulphuric acid cleaning mixture can also be sucked in with a rubber bulb.

meter of the rubber tube is placed in the latter. By pulling the rubber tube away from the ball with the thumb and forfinger of the left hand, a narrow clearing is made in the rubber tube, through which the liquid is discharged at a greater or lesser rate. The stopcock of the burette should be covered

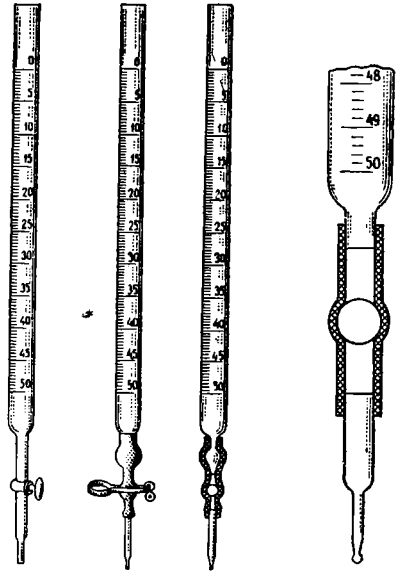


Fig. 29. Burettes

with a very thin layer of vaseline (petrolatum), making sure that none of it gets into the opening of the cock or into the burette.

Small volumes of liquid are measured by means of microburettes from 1 to 5 ml in capacity, graduated in 0.01-ml divisions.

Before filling a burette for the titration, it must be thoroughly washed, as even the slightest contamination causes drops of liquid to adhere to its walls and can lead to incorrect test results.

Burettes are washed, the same way as any other glassware, by filling them with dichromate-sulphuric acid cleaning

mixture. For this purpose place the burette upside down in a beaker containing cleaning mixture and, using a rubber bulb, suck in the mixture from the opposite end until the burette is completely filled. Close this end with the stopcock or pinch clip and allow the burette to stand in this position for 1-2 hours[1]. After that open the stopcock and drain the mixture back into the beaker. Then rinse the burette 5 or 6 times with tap water. If any drops remain on the wall of the emptied burette, it is necessary to repeat the procedure described above, using warm cleaning mixture.

Rinse the thoroughly washed burette 2 or 3 times with distilled water and then with the solution to be measured. Clamp the burette in a strictly vertical position and fill it with the appropriate solution to a height a little above the zero mark. On no account should there be any air bubbles in the stopcock or rubber tube. Air is removed by quickly opening the cock (clip) several times and delivering jets of the solution. Sometimes this is inadequate, in which case proceed as follows. Immerse the end of the burette provided with a stopcock into a beaker containing the solution; from the other end suck in the liquid to a height above the cock and close the latter. To free a burette with a rubber tube from air, turn up the tube with the capillary tip and open the clip. Drain the liquid through the upturned rubber tube and thus expell all the air from it. After removing the air, refill the burette to the top and then bring the level of the solution exactly to the zero mark by opening the stopcock or clip (it has already been mentioned that the observer's eyes must be level with the meniscus). To obtain the best conditions for reading off divisions, a white background (a sheet of white paper) is satisfactory, and it is even better to fit on the burette a strip of black paper so that its upper edge is 1 mm below the meniscus. Special burette readers are available now. Light-coloured liquids are measured by the lower meniscus, whereas dark-coloured ones, for example, $KMnO_4$, by the upper meniscus. However, if the burette with a dark solution is lighted from behind, the volume can

[1] Prior to washing burettes provided with a glass stopcock, the tap and socket are wiped free from grease with filter paper soaked in benzene or acetone.

be measured by the lower meniscus. It is important that during a given analysis all the readings be made in the same way, whether by the lower or upper meniscus.

CHAPTER XXXII

Calculations of Titrimetric Analysis

141. Gram-Equivalent

The gram-equivalent (g-equiv) of a substance is the number of grams of the reagent which in a given reaction corresponds to a gram-atom or gram-ion of hydrogen.[1]

It follows that the gram-equivalent of one and the same substance can be different in different reactions. For example, Na_2CO_3 reacts with an acid in two ways:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \quad (1)$$

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3 \quad (2)$$

In reaction (1) a gram-molecule of Na_2CO_3 reacts with a a gram-molecule of HCl which corresponds to one gram-atom of hydrogen.

In this reaction a gram-equivalent (g-equiv) of Na_2CO_3 is equal to one mole (M)[2] of Na_2CO_3, which is given by the equation.

$$E_{Na_2CO_3} = M_{Na_2CO_3} \quad 106.00 \text{ g}$$

In reaction (2) one gram-molecule of Na_2CO_3 reacts with 2 moles of HCl. Consequently,

$$E_{Na_2CO_3} = \frac{M_{Na_2CO_3}}{2} = \frac{106.00}{2} = 53.00 \text{ g}$$

In the reaction of $BaCl_2$ with Na_2SO_4:

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$$

$$E_{BaCl_2} = \frac{M_{BaCl_2}}{2} = \frac{208.3}{2} = 104.15 \text{ g}$$

since 1 mole of Na_2SO_4 corresponds to 1 mole of H_2SO_4 which contains 2 gram-atoms of hydrogen.

[1] The definition of the gram-equivalent of an oxidizing or reducing agent is given in Sec. 163.

[2] The designation for gram-equivalent in formulas is E. The designation for gram-molecule (mole) is M.

Questions and Problems

1. Define *gram-equivalent.*
2. Is the gram-equivalent of a substance a constant value? What does it depend on?
3. Calculate the gram-equivalent of the following substances in neutralization reactions: (a) NaOH; (b) H_2SO_4; (c) $Na_2CO_3 \cdot 10H_2O$; (d) $NaHCO_3$; (e) $Na_2B_4O_7 \cdot 10H_2O$.

Ans. (a) 40.00 g; (b) 49.04 g; (c) 143.07 g; (d) 84.01 g; (e) 190.69 g

4. Calculate the gram-equivalent of $KAl(SO_4)_2 \cdot 12H_2O$ in reactions of precipitation of K^+, Al^{3+}, SO_4^{2-} for: (a) potassium; (b) aluminium; (c) sulphate ion.

Ans. (a) 474.39 g; (b) 158.13 g; (c) 118.60 g

142. Normal and Molar Solutions

A normal solution, i.e., one that contains 1 g-equiv of dissolved substance (solute) in 1 litre of solution is denoted as $1N$.

Solutions containing 2, 0.5, 0.1, 0.01 g-equiv of solute in 1 litre are denoted respectively as $2N$, $0.5N$, $0.1N$, $0.01N$.

The normality of a solution (N) indicates the number of gram-equivalents of solute contained in 1 litre of solution or the number of milligram-equivalents of solute contained in 1 ml of solution.

The molarity of a solution (M) indicates the number of moles of solute contained in 1 litre of solution (*see* Sec. 2).

Example. 250 ml of a calcium hydroxide solution contain 3.705 g of $Ca(OH)_2$. Calculate the normality and molarity of the solution.

Solution. First find the number of grams of solute contained in 1 litre of solution:

$$\begin{array}{r} 3.705 \text{ g } Ca(OH)_2 \text{ are contained in } 250 \text{ ml} \\ x \text{ g } Ca(OH)_2 \text{ are contained in } 1000 \text{ ml} \\ \hline x = \dfrac{3.705 \times 1000}{250} = 14.82 \text{ g/lit} \end{array}$$

Find the gram-molecule and gram-equivalent:

$$M_{Ca(OH)_2} = 74.10; \; E_{Ca(OH)_2} = \frac{M_{Ca(OH)_2}}{2} = \frac{74.10}{2} = 37.05 \text{ g}$$

To calculate the normality, write the following proportion:

$$\begin{array}{l} 37.05 \text{ g/lit} - 1N \\ 14.82 \text{ g/lit} - xN \\ \hline x = \dfrac{14.82}{37.05} = 0.4N \end{array}$$

The molarity is found from the following proportion:

$$\begin{array}{l} 74.10 \text{ g/lit} - 1M \\ 14.82 \text{ g/lit} - xM \\ \hline x = \dfrac{14.82}{74.10} = 0.2M \end{array}$$

Questions and Problems

1. What is meant by a *normal solution* and a *molar solution*?
2. Express the concentration of $3N$ H_2SO_4 solution in: (a) grams per litre; (b) moles per litre; (c) gram-equivalents per litre.
Ans. (a) 147.1 g/lit; (b) 1.5 moles/lit; (c) 3 g-equiv/lit
3. How many grams of H_2SO_4 are contained in 1 litre of $0.15N$ solution?
Ans. 7.351 g
4. Express the concentration of $0.05N$ $Ca(OH)_2$ solution: (a) in moles per litre; (b) in g of CaO per 250 ml.
Ans. (a) $0.025M$: (b) 0.351
5. If 200 ml of sulphuric acid solution contain 2.450 g of H_2SO_4, calculate the molarity and normality of the solution.
Ans. (a) $0.125M$; (b) $0.2500N$
6. If 400 ml of soda solution contain 5.30 g of anhydrous sodium carbonate, calculate the normality of the solution.
Ans. $0.250N$

143. Titre of a Solution

The titre (T) of a solution is the number of grams of the dissolved substance (solute) contained in 1 ml of the solution.

The titre of a solution is denoted as T. For example, $T_{NaCl} = 0.005845$ g/ml indicates that each millilitre of the given sodium chloride solution contains 0.005845 g of NaCl. The titre of a solution can be calculated if its normality or molarity is known. For example, the titre of a molar H_2SO_4 solution containing in 1 litre 98.06 g of the acid is

$$T_{1M\ H_2SO_4} \parallel 0.09801 \text{ g/ml}$$

The titre of 0.1*N* H_2SO_4 solution is

$$T_{0.1N\ H_2SO_4} = 0.004901\ \text{g/ml}$$

The titre of a solution can be calculated from its known normality by the following formula:

$$T = \frac{E \cdot N}{1000}\ \text{g/ml}$$

The titre of a standard solution (titrant) can also be expressed in grams or milligrams of another substance (the one being determined), i.e., it defines what weight of the given substance is equivalent to 1 ml of the titrant.

For example, the titre of a 0.1*N* sulphuric acid solution expressed in grams of potassium hydroxide is equal to 0.00561 g/ml. This means that 1 ml of 0.1*N* sulphuric acid reacts with 0.00561 g of potassium hydroxide. This is written as follows:

$$T_{H_2SO_4/KOH} = 0.00561\ \text{g/ml}$$

and reads: *the titre of sulphuric acid in terms of potassium hydroxide is equal to* 0.00561 *g/ml.*

The titre of a standard solution in terms of the substance being determined is calculated from the following formula:

$$T_{\text{given solution (against the substance being determined)}} = \frac{E_{\text{substance being determined}} \cdot N_{\text{standard solution}}}{1000}$$

Example 1. Determine the titre of 0.1*N* H_2SO_4 solution against NaOH.

$$T_{0.1N\ H_2SO_4/NaOH} = \frac{E_{NaOH} \cdot N_{H_2SO_4}}{1000} = \frac{40.0 \times 0.1}{1000} = 0.0040\ \text{g/ml}$$

This means that 1 ml of 0.1*N* H_2SO_4 neutralizes 0.0040 g of NaOH.

Example 2. Determine the titre of 0.1*N* $AgNO_3$ solution in terms of NaCl.

$$T_{0.1N\ AgNO_3/NaCl} = \frac{E_{NaCl} \cdot N_{AgNO_3}}{1000} = \frac{58.44 \times 0.1}{1000} = 0.005844\ \text{g/m}$$

i.e., 1 ml of 0.1*N* $AgNO_3$ solution reacts with 0.005844 g of NaCl.

144. Corrections for Standard Solutions

Solutions used for titrating, whose exact concentration has been previously determined, are called *standard solutions* or *titrants*. The concentration of a standard solution is expressed by its normality, molarity, or titre.

Sometimes a *correction factor* or simply *correction K* is used for indicating the exact concentration of standard solutions. The correction shows the ratio of the normality of the given solution to a definite (standard) normality of such a value that the correction is close to unity.

The correction shows by what quantity the volume of the given solution must be multiplied to reduce it to the volume of the solution of a definite normality.

Example 1. A 0.1*N* HCl solution with $K = 1.146$ has a concentration 1.146 times that of a 0.1*N* solution and, therefore, 1 ml of such a solution is equivalent to 1.146 ml of 0.1*N* solution.

Example 2. If it is known that 21 ml of 0.1*N* NaOH ($K = 0.950$) was used to neutralize hydrochloric acid, determine the number of ml of exactly 0.1*N* solution used.

Solution. As 1 ml of the given solution is equivalent to 0.950 ml of 0.1*N* solution, 21 ml correspond to

$$21 \times 0.950 = 19.95 \text{ ml of } 0.1N \text{ solution}$$

If the weighed portion of the substance of chemically pure grade and the volume of the solution are known, the correction K can be found from the ratio

$$K = \frac{\text{actual weighed portion of C.P. solute}}{\text{calculated weighed portion of C.P. solute}}$$

Example 3. If 200 ml of solution was prepared from 1.3400 C.P. NaCl, find the correction for 0.1*N* NaCl solution.

Solution. 200 ml of an exactly 0.1*N* NaCl solution should contain

$$\frac{58.44 \times 0.1 \times 200}{1000} = 1.1688 \text{ g}$$

Wherefrom,

$$K = \frac{1.3400}{1.1688} = 1.146$$

The correction can be calculated as the ratio of the titre of the prepared solution to the titre of the solution of a definite normality:

$$K = \frac{\text{titre of the prepared solution}}{\text{titre of the solution of a definite normality}}$$

In the above example the titre of the prepared solution is

$$\frac{1.340}{200} = 0.00670 \text{ g/ml}$$

The titre of 0.1*N* NaCl solution = 0.005845; therefore,

$$K = \frac{0.00670}{0.005845} = 1.146$$

Obviously, if the correction for the given solution is greater than unity, its actual normality is greater than the normality taken as a standard; if the correction is less than unity, the actual normality of the solution is less than the standard normality.

Questions and Problems

1. Define the *titre* of a solution.
2. What solutions are called *standard solutions*?
3. Determine the titre of a solution if its molarity or normality is known. Give an example.
4. Calculate the titre of a 0.1*N* solution of the following substances: (a) HCl; (b) H_2SO_4; (c) KOH; (d) $Ca(OH)_2$; (e) $Na_2B_4O_7 \cdot 10H_2O$; (f) $H_2C_2O_4 \cdot 2H_2O$; (g) $H_2C_2O_4$.

Ans. (a) 0.003646 g/ml; (b) 0.004904 g/ml; (c) 0.005611 g/ml; (d) 0.003705 g/ml; (e) 0.01907 g/ml; (f) 0.006303 g/ml; (g) 0.004502 g/ml.

5. Calculate the titre of a 0.1*N* H_2SO_4 solution in terms of: (a) NaOH; (b) Na_2CO_3; (c) $NaHCO_3$; (d) CaO.

Ans. (a) 0.00400 g/ml; (b) 0.005300 g/ml; (c) 0.008401 g/ml; (d) 0.002804 g/ml.

145. Methods of Calculating

Several methods of calculation are used in titrimetric analysis.

1. Determination of normality of the solution under analysis from the normality of the standard solution. When two substances react, a gram-equivalent of one of the substances reacts with a gram-equivalent of the other. Solutions of dif-

ferent substances of the same normality contain in equal volumes of solution the same number of gram-equivalents of the solute. Consequently, equal volumes of such solutions contain equivalent quantities of substance. Thus, for example, to neutralize 30 ml of $1N$ H_2SO_4 solution it is necessary to use exactly 30 ml of $1N$ NaOH solution. Similarly, 30 ml of $0.12N$ KCl solution are needed for complete precipitation of ions contained in 30 ml of $0.12N$ $AgNO_3$ solution.

Solutions of the same normality react with each other in equal volumes.

If the normalities of the reacting solutions differ, different volumes of such solutions are used in the titration.

Solutions of different normality react with one another in volumes that are inversely proportional to their normalities.

If the normality of one of two reacting solutions and the volumes of the solutions used in the titration of one of the solutions with the other one are known, the unknown normality of the second solution can easily be determined.

Let us denote the normality of the first solution as N_1, its volume as V_1, the normality of the second solution as N_2, and its volume as V_2. Then we can write

$$\frac{N_1}{N_2} = \frac{V_2}{V_1}$$

wherefrom,

$$N_1 \cdot V_1 = N_2 \cdot V_2$$

Example 1. Determine the normality of a hydrochloric acid solution if it is known that 18.00 ml of $0.13N$ NaOH solution were used to neutralize 20.00 ml of the HCl solution.

Solution.

$$N_{HCl} \cdot V_{HCl} = N_{NaOH} \cdot V_{NaOH}$$

wherefrom,

$$N_{HCl} = \frac{N_{NaOH} \cdot V_{NaOH}}{V_{HCl}} = \frac{18.00 \times 0.13}{20\ 00} = 0.117N$$

If the normality of the standard solution is given with a correction, the concentration of the solution under test is also expressed by a correction to the same standard normality. If the volumes of the solutions used in the titration

are multiplied by the appropriate corrections, the volumes of the solutions of one and the same normality are obtained. We know that solutions of the same normality react in equal volumes. Therefore,

$$V_1 \cdot K_1 = V_2 \cdot K_2$$

and

$$K_2 = \frac{V_1 \cdot K_1}{V_2}$$

Example 2. If it is known that 23.00 ml of 0.1*N* HCl solution with $K = 1.050$ were used to neutralize 25.00 ml of NaOH solution, determine the concentration of the NaOH solution.

Solution.

$$V_{HCl} \cdot K_{HCl} = V_{NaOH} \cdot K_{NaOH}$$

Hence,

$$K_{NaOH} = \frac{V_{HCl} \cdot K_{HCl}}{V_{NaOH}} = \frac{23.00 \times 1.050}{25.00} = 0.966$$

2. Determination of content of the substance under test from the titre of the standard solution, expressed in grams of the substance being determined. The titre of the standard solution in grams of the substance being titrated is equal to the number of grams of the substance under test which is equivalent to the number of grams of solute contained in 1 ml of the standard solution.

The number of grams of the substance under analysis (mass *g*) can be calculated if the titre of the standard solution in terms of the substance being determined (see Sec. 143) and the volume of the standard solution used in the titration are known.

Example. A solution of a volume of 200 ml was prepared from a weighed portion of 1.2600 g of oxalic acid, and 15.00 ml of 0.1*N* NaOH solution were used in the titration of 20.00 ml of the above solution. Calculate the percentage of oxalic acid in the weighed portion.

Solution. The formula of oxalic acid is $H_2C_2O_4 \cdot 2H_2O$. The molecular mass $M_{H_2C_2O_4 \cdot 2H_2O} = 126.10$; the gram-equivalent $E_{H_2C_2O_4 \cdot 2H_2O} = 63.05$.

Hence,

$$T_{NaOH/H_2C_2O_4 \cdot 2H_2O} = \frac{63.05 \times 0.1}{1000} = 0.006305 \text{ g/ml}$$

The amount of oxalic acid contained in 20 ml of the prepared solution is equal to $0.006305 \cdot 15.00$ g.

The amount of oxalic acid in the graduated flask, i.e., in the weighed portion is

$$g = \frac{0.006305 \times 200 \times 15}{20}$$

The percentage of oxalic acid is equal to

$$\frac{0.006305 \times 15 \times 200 \times 100}{20 \times 1.26} = 75.04\%$$

Questions and Problems

1. In what ratio by volume do solutions of the same normality react?
2. In what ratio by volume do solutions of different normality react?
3. How many millilitres of 0.1*N* HCl solution are needed to neutralize: (a) 10.00 ml of 0.1*N* NaOH solution; (b) 10.00 ml of 0.1*N* $Ca(OH)_2$ solution; (c) 10.00 ml of 1*N* NaOH solution; (d) 10.00 ml of 0.5*N* $Ba(OH)_2$ solution; (e) 10.00 ml of 0.05*N* NH_4OH solution?

Ans. (a) 10.00 ml; (b) 10.00 ml; (c) 100.00 ml; (d) 50.00 ml; (e) 5.00 ml

4. How many millilitres of 0.3*N* $Ba(OH)_2$ solution is required to neutralize 45.00 ml of 0.51*N* H_2SO_4 solution?

Ans. 76.50 ml

CHAPTER XXXIII

Standard Solutions

146. Preparation of Standard Solutions

In order to prepare a standard solution of required concentration from a chemically pure substance, an accurately weighed portion of the latter is dissolved in a small quantity of water and the resulting solution diluted to a fixed volume.

To prepare, for example, a 0.1*N* solution of Na_2CO_3 (gram-equivalent of Na_2CO_3 = 0.5 mole = 53.00 g), weigh

out 5.3000 g of chemically pure Na_2CO_3, carefully transfer the weighed portion to a graduated flask, dissolve it in distilled water, and make up to 1 litre. Then close the flask with a stopper and mix the solution thoroughly.

When standard solutions are prepared from chemically pure substances, the portion weighed may be only approximately equivalent to the mass required by calculation, but it must be weighed to the nearest 0.0002 g. The normality of the resulting solution is then found by calculation.

Example 1. A portion of chemically pure Na_2CO_3 weighing 5.0257 g was transferred to a 1-litre graduated flask. After dissolving the soda in water, the solution was made up to the mark. Calculate the normality of the solution.

Solution. Write the proportion

$$\begin{array}{l} 5.3000 \text{ g } Na_2CO_3 — 0.1N \\ 5.0257 \text{ g } Na_2CO_3 — \ xN \end{array}$$

$$x = \frac{0.1 \times 5.0257}{5.3000} = 0.0948N$$

If the titre of the prepared solution (T_{sol}) is known, the normality of the solution can be calculated from it. In the given example

$$T_{sol} = \frac{5.0257}{1000} = 0.0050257 \text{ g/ml}$$

The titre of $1N$ Na_2CO_3 solution is equal to

$$T_{1N} = \frac{53.000}{1000} = 0.053000 \text{ g/ml}$$

Hence,

$$N = \frac{0.0050257}{0.053000} = 0.0948N$$

Most standard solutions have to be prepared from substances containing impurities. Sodium hydroxide, for example, is hygroscopic and rapidly absorbs CO_2 from the air, being partly converted to the carbonate.

The concentration of a solution prepared from a weighed portion of such a substance will only be approximate. The exact concentration of such a solution is not determined from the mass of the weighed portion but is found by titrating the solution with another solution of known concentra-

tion. This process is called *standardization* against a primary standard. For instance, a standard solution of chemically pure oxalic or succinic acid is used to determine the concentration of a NaOH solution. For this purpose, weigh out accurately on an analytical balance a portion of one of the above acids, carefully transfer it to a measuring flask, and dilute to the mark with water. After mixing the solution thoroughly, pipette a fixed volume into a conical flask, and titrate with the prepared NaOH solution in the presence of 2 or 3 drops of phenolphthalein indicator to determine the volume of the alkali solution equivalent to the acid solution taken for titration. Then calculate the normality of the alkali solution:

$$\frac{\text{volume of alkali}}{\text{volume of acid}} = \frac{N_{acid}}{N_{alkali}}$$

The concentration of the solution can also be determined by titrating with it a weighed portion of chemically pure substance dissolved in any suitable volume of water. In this case the entire solution is titrated.

A solution of a given normality can be obtained by first preparing a solution of a concentration higher than that required, determining its normality, and then calculating the volume of water that must be added to 1 litre of this solution to obtain a solution of the required concentration. After adding this volume of water, the normality of the solution is checked by titration.

Example 2. How much water must be added to 1 litre of $0.125N$ alkali solution in order to obtain a $0.1N$ solution?

Solution. Determine how many times the solution must be diluted:

$$\frac{0.125}{0.1} = 1.25 \text{ times}$$

Therefore, after diluting 1 litre of the $0.125N$ solution, 1.250 litres of $0.1N$ solution should be obtained, i.e., 250 ml of water must be added to 1 litre of the $0.125N$ solution.

This problem can be solved by means of the ratio between the volumes and normalities of the original and final solutions:

$$\frac{V_1}{V_2} = \frac{N_2}{N_1}; \quad \frac{x}{1000} = \frac{0.125}{0.1}; \quad x = \frac{0.125 \times 1000}{0.1} = 1250 \text{ ml}$$

Hence, 1 litre of the 0.125*N* solution (prepared at first) must be diluted with 250 ml of water to obtain a 0.1*N* solution.

Standard solutions are liable to change their concentration on standing; therefore, they should be kept in bottles closed with stoppers carrying a guard tube filled with soda

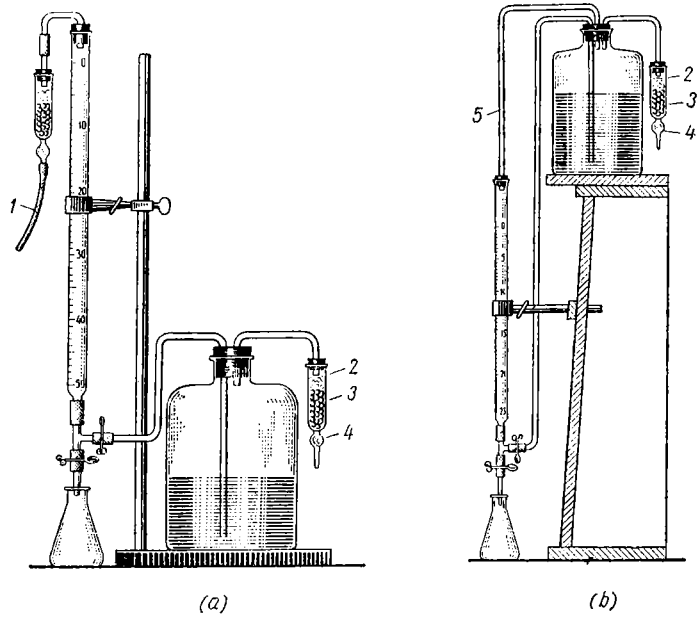


Fig. 30. Apparatus for standard solutions

1 — tube for sucking in the solution; *2* — cotton wool; *3* — soda lime; *4* — cotton wool; *5* — siphon tube

lime (Fig. 30). The solution should be restandardized at necessary intervals. The burette used in the titration should be connected directly to this bottle.

When the apparatus for titration shown in Fig. 30*a* is used, the burette is filled with the standard solution through a rubber tube by expelling the air from the burette by suction (with the pinch clip on the branch tube open) or by forcing air into the bottle containing the standard solution by means of a rubber bulb. When the apparatus shown

in Fig. 30*b* is used, the bottle is placed above the burette so that the top of the latter is always lower than the bottom of the solution bottle. To fill the burette, it is sufficient to open the clip on the branch tube.

The bottle should be labelled with the chemical formula of the solute, the normality of the standard solution, the date it was determined, and the name of the operator who determined the normality.

147. Preparation of Standard Solutions from Primary Standards, 'Fixinals'

Fixinals are factory-made or laboratory-prepared glass ampoules containing a definite number of gram-equivalents of chemically pure substance in the form of a solid or solution. Usually an ampoule contains 0.1 or 0.01 gram-equivalent of a substance. Most fixinals do not change on standing; some of them, however, do change gradually with time. Sodium hydroxide solutions, for example, become turbid in 2-3 months due to the action of the alkali on the glass.

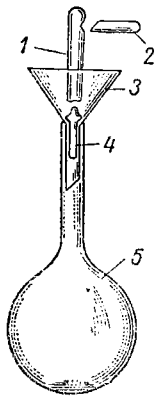


Fig. 31. Apparatus for preparing solutions from primary substances in ampoules ('fixinals')

1 — ampoule; *2*, *4* — punchers; *3* — funnel; *5* — graduated flask

The standard solution is prepared from the fixinal and its normality determined by transferring the contents of the ampoule quantitatively to a graduated flask and diluting the solution with distilled water to the mark. This is done as follows. First wash the punchers (provided in the box with the ampoules) with tap water then with distilled water. Place puncher *4* (Fig. 31) in clean chemical funnel *3* so that its long end enters the neck of the funnel and the short (sharp) end is directed upwards; the cross-shaped ribs rest on the lower end of the funnel cone. Place the funnel together with the puncher in clean graduated flask *5*. First wash ampoule *1* from the outside with warm water and then with cold distilled water to wash off the label and any dirt on the ampoule. Then invert it

and, striking the bottom depression in it against the puncher in the funnel, break the bottom of the ampoule. Still holding the latter over the funnel, pierce the top depression in it with puncher *2*, drain the contents of the ampoule into the graduated flask, place the drawn-out capillary tip attached to the delivery tube of the wash bottle in the hole at the top, and wash down the inside of the ampoule with a jet of water. Use the wash bottle to wash the outer surface of the ampoule and the funnel with the puncher and then remove the funnel from the flask. Make up the volume of the liquid to the mark. Tightly stopper the flask and invert it many times to ensure thorough mixing.

Problems

1. Calculate the weighed portion required to prepare 2.5 litres of 0.5*N* solutions of each of the following substances: (a) KNO_3; (b) Na_2SO_4; (c) $Ca(OH)_2$.

Ans. (a) 126.4 g; (b) 88.78 g; (c) 46.31 g

2. What quantity of chemically pure $Na_2B_4O_7 \cdot 10H_2O$ is required to prepare 200 ml of 0.1*N* solution?

Ans. 3.8138 g

3. Determine the normality of a NaCl solution that contains 2.9230 g of NaCl in 200 ml of solution.

Ans. 0.25*N*

4. An aqueous solution was prepared from 5.3000 g of chemically pure $H_2C_2O_4 \cdot 2H_2O$ in a 500-ml flask. Determine the normality of the resulting solution.

Ans. 0.1682*N*

5. How much water must be added to 1 litre of 0.250*N* HCl solution to obtain a 0.2*N* solution?

Ans. 250.0 ml

148. Dilution of Solutions

It is often necessary to prepare a solution of required concentration from a more concentrated solution. For this purpose first calculate how much of the available solution must be taken to obtain a solution of the required concentration. The more concentrated solution can be diluted with water or a solution of lower concentration than that required.

Example 1. In what ratio by weight must a 60 per cent and 35 per cent solution of nitric acid be mixed to obtain a 45 per cent solution.

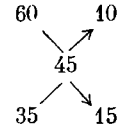
Solution. If we denote the mass of the 60 per cent solution as X and the mass of the 35 per cent solution as Y, the amount of HNO_3 in the first solution will be $0.60X$; in the second $0.35Y$; in all, $0.60X + 0.35Y$. The mass of the 45 per cent solution is $(X + Y)$ and the amount of HNO_3 in it equals $0.45\ (X + Y)$. This amount of HNO_3 is contained in the volumes of 60 and 35 per cent acid solutions taken, i.e., in $0.60X + 0.35Y$. Write and solve the following equation:

$$0.60X + 0.35Y = 0.45\ (X + Y)$$

$$0.60X + 0.35Y = 0.45X + 0.45Y$$

Wherefrom, $0.15X = 0.10Y$ or $X : Y = 0.10 : 0.15 = 10 : 15 = 2 : 3$.

Therefore, to obtain a 45 per cent solution it is necessary to mix two parts by weight of the 60 per cent solution and 3 parts by weight of the 35 per cent solution. The same result is obtained by the crosswise rule:



The numerical values of the concentrations of the available solutions are written on the left-hand side of the scheme, one under the other; the value of the required concentration is written in the centre. This value is subtracted from the larger number ($60 - 45 = 15$). This difference is written in the direction of the arrow to the right of the lower concentration. The value of the lower concentration (35) is subtracted from the value of the required concentration (45) and the difference (10) is written in the direction of the arrow to the right of the higher concentration. The ratio of the numbers written on the right-hand side shows the ratio of the masses of the available solutions that must be taken to obtain a solution of the required concentration. Thus, to obtain a 45 per cent HNO_3 solution, the 60 and 35 per cent solutions must be mixed in the ratio of 10 : 15, i.e., 2 : 3.

Example 2. In what ratio by weight must an 80 per cent H_2SO_4 solution be mixed with water to obtain a 30 per cent sulphuric acid solution?

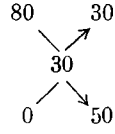
We must mix X g of 80 per cent H_2SO_4 with Y ml of water or Y g of water (which is the same). Obviously the mass of a 30 per cent solution is equal to $X + Y$; it contains $0.3\ (X + Y)$ g of H_2SO_4. As in the previous example, we can write the following equation:

$$0.8X = 0.3\ (X + Y), \quad \text{or} \quad 0.5X = 0.3Y$$

Wherefrom, $X : Y = 0.3 : 0.5 = 3 : 5$.

Hence, five parts by weight of water must be added to every three parts by weight of 80 per cent sulphuric acid.

We may also make use of the crosswise rule. Water will be considered to be a solution with a concentration equal to zero:



From the scheme obtained, it follows that the ratio by weight of 80 per cent sulphuric acid and water equals 30 : 50 or 3 : 5.

Problems

1. How many millilitres of water must be added to 1 litre of $0.16N$ HCl solution to obtain $0.1N$ HCl solution?

Ans. 600 ml

2. A $6N$ H_2SO_4 solution is available. How many millilitres of this solution are required to obtain 160 ml of $2N$ solution by dilution with water?

Ans. 53.33 ml

3. The titre of a $H_2C_2O_4 \cdot 2H_2O$ solution is equal to 0.0100 g/ml. To what volume must 200 ml of this solution be diluted to obtain a 0.05 N solution?

Ans. 634.8 ml

4. How many millilitres of $12N$ HCl solution are required to obtain 1 litre of $3N$ acid by dilution with water?

Ans. 250 ml

CHAPTER XXXIV

Acid-Base Titrations

149. Principles of Acid-Base Titrations

The basic reaction in this method is neutralization, i.e., the interaction of an acid and base. It is expressed by the equation

$$H^+ + OH^- = H_2O$$

The standard solution may be an acid or a base, depending on what is titrated.

This method is used mainly for the quantitative determinations of acids and bases. It can also be used to determine water hardness, the concentration of ammonium salts and salts of weak acids, such as Na_2CO_3 and $Na_2B_4O_7$. Aqueous solutions of such salts, due to hydrolysis, have an alkaline reaction and may therefore be titrated with an acid.

150. Indicators Used in Acid-Base Titrations

The indicators used in acidimetry and alkalimetry are substances that change their colour depending on the hydrogen ion concentration of the solution. The colour of the solution often depends on whether it contains undissociated molecules of the indicator or the same substance dissociated into ions. Therefore, the indicators generally used here are weak organic acids or bases, the molecular and ionized forms of which are of a distinctly different colour. There are also indicators that are neither acids nor bases. The change in their colour is due to rearrangement of atoms in the molecules, when the hydrogen ion concentration of the solution changes, to form chromophores of different colours.

If the indicator is a weak acid, it can be denoted as HIn. Such an indicator dissociates into ions according to the equation

$$\underset{\text{acid form}}{HIn} \rightleftarrows H^+ + \underset{\text{basic form}}{In^-}$$

In an acidic solution this indicator is in the undissociated state due to the common ion effect (H^+) and the colour

of the indicator is determined by the colour of the undissociated HIn molecule (the acid form of the indicator). If the same indicator is added to a base, it is strongly dissociated. Hence, its colour in an alkaline solution is due to the colour of the In^- anion (the alkaline form of the indicator). The colour of the indicator in solutions with different hydrogen ion concentrations depends on the ratio of the concentration of the ions of the indicator and its undissociated molecules, i.e., on the ratio of its acid form to its alkaline form:

$$\frac{[HIn]}{[In^-]}$$

Thus, a definite number of undissociated molecules of the indicator corresponds to different hydrogen ion concentrations in each solution. Since the colour of undissociated molecules of an indicator differs from that of its ions, the solution assumes the colour of undissociated molecules or its ions depending on which form predominates.

Solutions of colourless acids in the presence of an indicator assume a colour that is characteristic of undissociated molecules of the indicator. As the alkali solution is added to the acid, the concentration of hydrogen ions in the solution decreases and, therefore, the number of molecules of the indicator dissociated into ions increases. This explains the gradual change in the colour of the solution.

The transition range of an acid-base indicator is determined by the pH range over which the colour change of an indicator takes place. For instance, methyl orange exhibits its colour change within a pH range from 3.1 to 4.4. This means that in solutions in which the pH is equal to or less than 3.1 the indicator has a different colour (red-orange) than in solutions with a pH equal to or more than 4.4 (yellow). Solutions with a pH less than 4.4 but more than 3.1 are coloured by methyl orange by a transitional pale orange colour.

This can be illustrated by the following experiment. Prepare an approximately 0.002*N* HCl solution with a pH = = 2.7. Pour into each of three 200-ml graduated cylinders different quantities of the acid solution: 50, 17, and 2.5 ml and dilute each solution to 100 ml. The solution in the first cylinder will have a concentration of $[H^+] = 10^{-3}$ and pH = = 3; the solution in the second cylinder, $[H^+] = 3.4 \cdot 10^{-4}$

and pH = 3.47; in the third cylinder, $[H^+] = 5 \cdot 10^{-5}$ and pH = 4.3. After adding 1 or 3 drops of methyl orange, the solution in the first cylinder will be pink; in the second cylinder, pale orange; in the third cylinder, yellow.

Indicators Most Commonly Used for Acid-Base Titrations

Indicator	Colour of solution		pH range at transition	Preparation of indicator solution
	in acidic solution	in alkaline solution		
Methyl orange	Red-orange	Yellow	3.1-4.4	0.05 g in 100 ml of water
Methyl red	Red	Yellow	4.2-6.2	0.2 g in 100 ml of ethanol
Litmus	Red	Blue	5.0-8.0	1.9 g in 100 ml of water
Neutral red	Red	Yellow	6.8-8.0	0.1 g in 70 ml of ethanol + 30 ml of water
Phenolphthalein	Colourless	Red-violet	8.2-10.0	1 g in 100 ml of ethanol
Thymolphthalein	Colourless	Blue	9.3-10.5	0.1 g in 100 ml of ethanol

Of all the indicators listed in the Table, only neutral red changes its colour at the moment when the solution becomes neutral (6.8 to 8.0); the other indicators change their colour either in acidic solution (methyl orange) or in alkaline solution (phenolphthalein). Since titration is continued until the indicator changes colour, titration, as a rule, does not end at the moment of neutralization, but when the solution is slightly acidic or weak-alkaline, i.e., at a concentration of hydrogen ions that hardly ever coincides with the equivalence point. Therefore, there is inevitably an indicator error. In order that this error be minimum, it is necessary to use the most suitable indicator for each given titration.

pT-value. The most important characteristic of an acid-base indicator is its pT-value, i.e., the concentration of hydrogen ions at which the sharpest change in colour of the indicator occurs. Usually, the titrant is added to the solution under test until the colour of the indicator changes abruptly. The value of the pT is numerically equal to the pH at

which this sharp change in colour occurs. The pT-value of the indicator is equal to or close to the concentration of hydrogen ions at the equivalence point.

The pT-value is approximately in the middle of the transition range. Each indicator is characterized by its transition range and its pT-value. The indicators most commonly used for acid-base titrations have the following pT-values:

Indicator	Methyl orange	Methyl red	Litmus	Phenolphthalein
pT-value	4	5	7	9

151. Correct Choice of Indicator

The chief requirement that should be met when selecting the most suitable indicator for a particular acid-base titration is that the pH range in which the indicator changes in colour be as close as possible to the pH of the unknown solution at the equivalence point. It is therefore necessary to determine the pH-value at the equivalence point.

Of all the indicators available, the one chosen should have a pT-value that differs as little as possible from the pH of the unknown solution at the equivalence point.

Let us consider the most common cases of acid-base titrations. The standard solutions used in the titration are usually solutions of strong acids or alkalies.

Titration of a strong acid with a strong base or a strong base with a strong acid. When hydrochloric acid is titrated with standard sodium hydroxide solution, or sodium hydroxide with standard hydrochloric acid, the solution at the equivalence point contains NaCl, a salt formed by a strong acid and a strong base. As we already know, such salts are not hydrolyzed; therefore, the pH of the solution at the equivalence point is equal to 7. Apparently, when titrating a strong acid with a strong base or vice versa, the indicator used should have a pT equal to 7 (for example, neutral red). However, in such cases it is possible to use indicators that change in colour in pH ranges from 4 to 10, since the indica-

tor error will not be greater than 0.125 per cent. Thus, almost all the above-mentioned indicators can be used.

It can be proved that on using any of these indicators the error will not exceed 0.125 per cent. Let us titrate, for instance, 20 ml of 0.1*N* HCl solution with 0.1*N* NaOH solution. Suppose that in one case 19.95 ml of 0.1*N* of NaOH is added and in another, 20.05 ml of the same solution. Prior to titration, the solution contains 20 ml of 0.1*N* HCl solution or 2 mg-equiv HCl (20×0.1). On adding 19.95 ml of 0.1*N* NaOH solution, 0.005 mg-equiv of the acid ($20 \times 0.1 - 19.95 \times 0.1 = 0.005$) is not neutralized; on adding 20.05 ml of 0.1*N* NaOH solution, 0.005 mg-equiv of the hydroxide ($20.05 \times 0.1 - 20 \times 0.1 = 0.005$) is not neutralized.

In both cases the solution contains an excess of 0.005 mg-equiv of acid or base in approximately 40 ml of solution ($20 + 19.95 = 39.95$ ml or $20 + 20.05 = 40.05$ ml). Hence, in each millilitre of solution there is an excess of acid or base equal to

$$\frac{0.005}{40} = 0.000125 \text{ mg-equiv}$$

and the indicator error will be

$$\frac{0.000125 \times 100}{0.1} = 0.125\%$$

Let us calculate the pH of the resulting solutions.

(a) On adding 19.95 ml of 0.1*N* NaOH solution to 20 ml of 0.1*N* HCl solution, we obtain 39.95 ml of a solution containing 0.005 mg-equiv of acid. The normality of the acidic solution will equal

$$\frac{0.005}{39.95} = 0.000125N$$

The concentration of hydrogen ions in this solution is equal to the concentration of the acid, i.e., $[H^+] = 0.000125 = 1.25 \cdot 10^{-4}$ g-ion/lit, wherefrom $pH = 4 - \log 1.25 = 4 - 0.1 = 3.9$.

(b) On adding 20.05 ml of 0.1*N* NaOH solution to 20 ml of the 0.1*N* HCl solution, we obtain 40.05 ml of a solution containing 0.005 mg-equiv of NaOH. The normality of the

alkaline solution will be

$$\frac{0.005}{39.95} = 0.000125N$$

The concentration of hydroxyl ions is equal to the concentration of the hydroxide.
Hence,

$$[OH^-] = 0.000125 = 1.25 \cdot 10^{-4} \text{ g-ion/lit}$$
$$pOH = 4 - \log 1.25 = 3.9$$
$$pH = 14 - 3.9 = 10.1$$

Therefore, allowing an error of not more than 0.125 per cent, titration is ended at a pH from 3.9 to 10.1, i.e., within the range of the pT-values of all the indicators mentioned above.

Titration of a weak acid with a strong base. Let us titrate acetic acid with sodium hydroxide ($CH_3COOH + NaOH$). At the equivalence point the solution will contain CH_3COONa, a salt formed by a weak acid and strong base. As a result of hydrolysis of the salt, the solution will have an alkaline reaction. Titration in this case should be ended in an alkaline solution (pH greater than 7). Therefore, the indicator used should change in colour at a pH > 7. Phenolphthalein is such an indicator. Thus, when titrating 0.1*N* CH_3COOH solution with 0.1*N* NaOH solution, at the equivalence point, a 0.1*N* CH_3COONa solution is obtained with a pH = 8.87; this almost coincides with the pT-value of phenolphthalein. If methyl orange is used, the pT-value lies between 3.1 and 4.4 and the indicator error will be about 50 per cent.

Titration of a weak base with a strong acid. For example, ammonium hydroxide is titrated with hydrochloric acid ($NH_4OH + HCl$). In this case, at the equivalence point the solution will contain NH_4Cl, a salt formed by a strong acid and a weak base. As a result of hydrolysis of this salt, the solution has an acid reaction at the equivalence point. Hence, in such cases only those indicators can be used which change in colour at a pH less than 7. The most suitable indicators are methyl orange and methyl red. Thus, on titrating 0.1*N* NH_4OH solution with 0.1*N* HCl solution, a 0.05*N* NH_4Cl solution will be formed at the equivalence point;

the pH of this solution is equal to 5.28 which is close to the pT-value of methyl orange and methyl red indicators.

The various conditions of titration and indicators used are given in the following Table.

Conditions of titration	pH at equivalence point	Indicator used
1. Strong acid with strong base	7	Methyl orange, methyl red, phenolphthalein
2. Strong base with strong acid	7	Methyl orange, methyl red, phenolphthalein
3. Weak acid with strong base	>7 (weak-alkaline solution)	Phenolphthalein
4. Weak base with strong acid	<7 (slightly acidic solution)	Methyl red, methyl orange

CHAPTER XXXV

Acid-Base Titration Procedures

152. Preparation of Standard Solutions of Acids and Bases

Preparation of standard acid solution. A concentrated acid solution is diluted to the required concentration with water.

Find the approximate concentration of an available acid solution with the aid of an areometer (hydrometer) and reference table as follows. Pour the concentrated solution into a tall glass cylinder with a diameter at least twice as large as the bulb of the areometer. Carefully immerse the areometer in the liquid and see that it floats freely without touching the walls of the cylinder. Read off the areometer scale. The division of the scale that coincides with the level of the liquid indicates the density of the solution. The percentage of the acid contained in the solution is found from Tables (see Appendix 4); from the concentration in per cent, calculate the titre of the solution, i.e., the number of grams of

solute in 1 ml of solution, or the normality, i.e., the number of gram-equivalents contained in 1 litre of solution.

The titre and normality of the acid is calculated from the following formulas:

$$T = \frac{a \cdot d}{100}; \qquad N = \frac{a \cdot d \cdot 1000}{100 \cdot E} = \frac{10ad}{E}$$

where T = titre of the solution;
N = normality of the acid solution;
a = percentage of acid;
d = density of the solution;
E = gram-equivalent of the acid.

After determining the titre or normality of the concentrated acid solution, calculate the volume of the original acid that must be used to prepare the solution of desired concentration.

Example. It is necessary to prepare 5 litres of 0.1N HCl solution from concentrated hydrochloric acid.

Determine the density of the acid with the aid of an areometer. It is equal to 1.19 g/cm^3. In accordance with the Table given in Appendix 4, acid of density of 1.19 g/cm^3 contains 38.0 per cent HCl. Further, calculation is carried out in one of the following ways.

Method 1. Find the mass of hydrogen chloride that is required to prepare 5 litres of 0.1N HCl solution, taking into account that

$$E_{HCl} = M_{HCl} = 36.46 \text{ g (rounded off to 36.5 g)}$$

The mass of hydrogen chloride that is required to prepare the solution is

$$\frac{36.5 \times 5}{10} = 18.25 \text{ g}$$

The titre of the original acid solutions is

$$T_{HCl} = \frac{38.0 \times 1.19}{100} = 0.4522 \text{ g/ml}$$

Since to prepare 5 litres of 0.1N acid solution it is necessary to dissolve 18.25 g of hydrogen chloride, take $\frac{18.25}{0.45} \approx$ $\approx$ 40.5 ml (density 1.19 g/cm^3) of 38 per cent hydrochloric

acid. Measure off 40-41 ml of acid with a graduated cylinder and dilute the solution to 5 litres.

Method 2. Write and solve the following proportion:

100 g of the original acid solution contain 38 g of C.P. HCl
x g of the original acid solution contain 18.25 g of C.P. HCl

$$x = \frac{100 \times 18.25}{38} = 48.03 \text{ g of chemically pure HCl}$$

In order to measure off the hydrochloric acid in a graduated cylinder instead of weighing it, we must calculate the volume of 38 per cent acid needed to prepare the required solution. This is done by dividing the mass of the HCl (38 per cent acid) by its density:

$$\frac{48.03}{1.19} \approx 40.4 \text{ ml}$$

Method 3. Calculate the normality of the original acid solution:

$$N_{HCl} = \frac{38.0 \times 1190}{36.46 \times 100} = 12.40N$$

We can find the volume of the acid (density 1.19 g/cm^3) from the formula $V_1 \cdot N_1 = V_2 \cdot N_2$:

$$V_2 = \frac{V_1 \cdot N_1}{N_2} = \frac{5000 \times 0.1}{12.40} \approx 40.3 \text{ ml}$$

The normality of the resulting HCl solution, in all cases, is additionally determined by titration with a standard solution of chemically pure borax (see Sec. 155) or anhydrous sodium carbonate (see Sec. 156).

Preparation of standard alkali solution. A solution of a strong alkali rapidly absorbs carbon dioxide from the air; therefore, it is always contaminated with carbonate. The presence of carbonate in the hydroxide solution complicates titration and introduces an error in the analysis, especially if phenolphthalein is used as indicator. Care should be taken to remove carbonate from the alkali used to prepare the standard solution. Water for the standard solution must be freed from the carbon dioxide dissolved in it by boiling during 0.5-1 hour. Place a few glass capillary tubes fused at one end in the flask with water, so that it boils gently.

Then cool the water in the flask in which it was boiled or in the bottle in which the standard solution is to be kept. The bottle should be previously rinsed with warm water so that it does not crack.

Close the bottle (or flask) containing the water at once with a stopper carrying a soda-lime guard tube to absorb CO_2 from the air. Then weigh out the alkali in a porcelain dish in an amount exceeding by 10 per cent the amount calculated. Wash the surfaces of the pieces of alkali in the dish with distilled water; this frees the alkali from most of the carbonate which is mainly on the surface. Quickly transfer the washed alkali to the bottle containing a measured volume of CO_2-free water, dissolve it completely in the water and add 20-30 ml of 10 per cent $BaCl_2$ solution to precipitate traces of carbonate,[1] agitate the solution thoroughly and allow the precipitate of $BaCO_3$ to settle.

Keep the prepared solution in the bottle protected from the atmosphere by a soda-lime guard tube (see Fig. 30).

The exact normality of the solution prepared is determined by standardizing it against chemically pure succinic or oxalic acid (see Sec. 157).

Problems

1. Determine the value of the gram-equivalent of the following substances in neutralization reactions: (a) HNO_3; (b) H_2SO_4; (c) KOH; (d) $Ca(OH)_2$; (e) Na_2CO_3; (f) $Na_2CO_3 \cdot 10H_2O$; (g) $NaHCO_3$; (h) $Na_2B_4O_7 \cdot 10H_2O$.

2. Calculate the normality and titre of the following solutions: (a) HCl, density 1.108 g/cm ^{3}; (b) H_2SO_4, density 1.814 g/cm^3; (c) NH_4OH, density 0.904 g/cm^3.

Ans. (a) 6.68*N*, 0.244 g/ml; (b) 33.29*N*, 1.633 g/ml; (c) 13.83*N*, 0.235 g/ml

3. What is the titre of a decinormal solution of HCl in terms of grams of each of the following substances: (a) HCl; (b) NaOH; (c) Na_2CO_3; (d) $Ba(OH)_2$.

Ans. (a) 0.003646 g/ml; (b) 0.0040 g/ml; (c) 0.005304 g/ml; (d) 0.00857 g/ml

4. What volume of H_2SO_4 of density 1.202 g/ml must be diluted with water to obtain 3 litres of 0.1*N* acid?

Ans. 43.7 ml

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[1] A small excess of $BaCl_2$ does not affect the accuracy of titration with the sodium hydroxide.

153. Recrystallization of Borax

Decahydrate borax, $Na_2B_4O_7 \cdot 10H_2O$, is used to standardize acid solutions. Borax, depending on the conditions of crystallization, can form crystals with a smaller number of molecules of water, for example, $Na_2B_4O_7 \cdot 2H_2O$. In order to obtain homogeneous crystals of the decahydrate, it is necessary to recrystallize commercial borax under specified conditions as follows. Heat water to 70°C and prepare in it a saturated solution of borax.[1] For this purpose dissolve, stirring constantly, approximately 12 g of finely ground borax per 100 ml of water; keep the temperature of the solution at 65-70°C. Quickly filter the resulting solution through a folded filter-paper using a funnel for hot filtration (see Fig. 16). Slowly cool the filtered solution to 25-30°C. Then place the vessel containing the solution in cold water. Stir the solution with a glass rod to accelerate crystallization. The precipitated crystals of borax are separated by filtration through a Buchner funnel (see Fig. 17), applying suction, and dried between sheets of filter paper until the crystals readily come loose from the dry stirring rod used to mix it.

Recrystallized borax should be kept in a jar with a ground-glass stopper in order to avoid efflorescence.

As borax is only moderately soluble at room temperature, solutions not stronger than 0.25*N* are prepared for standardizing acid solutions. More concentrated solutions are standardized with calcined chemically pure sodium carbonate, Na_2CO_3.

154. Preparation of Chemically Pure Anhydrous Sodium Carbonate

Chemically pure anhydrous sodium carbonate, Na_2CO_3, is obtained from commercial sodium bicarbonate, $NaHCO_3$, which is purified by recrystallization as follows. Dissolve in boiling water 15 g of sodium bicarbonate per 100 ml of water.[2] Filter the hot solution through a folded filter placed

[1] At 20°C, 5 g of $Na_2B_4O_7 \cdot 10H_2O$ dissolve in 100 ml of water.
[2] At 20°C, 9.6. g of $NaHCO_3$ dissolve in 100 ml of water.

in a funnel for hot filtration. Collect the filtrate in a beaker immersed in cold water. Stir the contents of the beaker with a glass rod. The precipitated crystals of $NaHCO_3$ are separated from the solution by filtering through a Buchner funnel (applying suction), then pressed between sheets of filter paper, and dried in a drying cabinet at a temperature of approximately 120°C.

Place the dried crystals in a crucible (preferably a platinum crucible); the layer of crystals should be not greater than 2-3 cm. Calcine the crucible for 30-40 minutes on a slow burner flame. From time to time mix the mass being calcined with a thick platinum wire. The temperature in the crucible should not exceed 300°C. Calcine to constant mass. Instead of calcining in a flame, the crucible can be dried for 2-3 hours in a drying cabinet (at 270-300°C). Keep the resulting product in a weighing bottle placed in a desiccator.

155. Standardization of Hydrochloric Acid Against Chemically Pure Borax

Chemically pure $Na_2B_4O_7 \cdot 10H_2O$ is suitable for standardizing strong acids because of a number of advantages it has over other substances: the chemically pure product is readily obtained by recrystallization from aqueous solutions; it is adequately stable in the air as it is not hygroscopic; error in weighing is minimum because of its high molecular weight.

Borax is the salt of a strong base and a weak acid, and therefore, as a result of hydrolysis, its reaction is alkaline ($pH > 7$). On reacting with a strong acid, it forms boric acid, H_3BO_3:

$$Na_2B_4O_7 + 2HCl = 2NaCl + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O = 4H_3BO_3$$

On adding these two equations we obtain

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

H_3BO_3 is a weak acid. The concentration of hydrogen ions in 0.1*N* solution (considering only the first stage of disso-

ciation) is equal to

$$[H^+] = \sqrt{K'_{H_3BO_3} \cdot C_{H_3BO_3}} = \sqrt{5.8 \cdot 10^{-10} \cdot 0.1} = 7.61 \cdot 10^{-6}$$

Hence,

$$pH = 6 - \log 7.61 = 6 - 0.88 = 5.12$$

Since methyl orange in aqueous solutions still has a yellow colour at pH = 5.12 (the pT-value of methyl orange is equal to 4), the colour of the solution will change only in the presence of a small excess of hydrochloric acid. Therefore, when standardizing a strong acid against borax in the presence of methyl orange, the indicator error will not be greater than the permissible one.

The hydrochloric acid solution can be standardized by titrating with it a fixed volume of borax solution of exactly known concentration or solutions prepared from separate weighed portions of borax.

Standardization of the acid against a fixed volume of borax solution. Prepare a solution of chemically pure borax of a definite concentration as follows. Calculate the amount of chemically pure $Na_2B_4O_7 \cdot 10H_2O$ required to prepare a solution of a normality that is approximately equivalent to the normality of the acid solution. $E_{Na_2B_4O_7 \cdot H_2O}$ is equal to 190.69 g; therefore, 19.069 g/lit are needed to prepare a 0.1*N* solution. To prepare 200 ml of 0.1*N* solution (the capacity of the graduated flask) it is necessary to take 19.069:5 = 3.8138 g of borax.

Procedure. Weigh out in a previously weighed beaker 3-4 g of chemically pure borax. Dissolve the weighed portion in hot water. Carefully transfer the solution to a graduated flask through a funnel, washing the beaker and funnel with hot water several times and collecting the wash water in the same graduated flask. Mix the contents of the flask by swirling. Make sure that the weighed portion is completely dissolved and allow the solution to cool down to room temperature. Make up to the mark with water, close the flask tightly with its stopper and mix the solution thoroughly.

Determine the normality of the borax solution from the mass of the weighed portion.

Example 1. If 200 ml of solution were prepared from 3.7580 g of chemically pure borax, what is the normality of the solution?

The titre of the solution equals $\frac{3.7580}{200} = 0.01879$ g/ml. The titre of 1*N* borax solution is 0.19069 g/ml. Write the following proportion:

$$\begin{array}{c} 0.19069 \text{ g/ml} - 1N \\ 0.01879 \text{ g/ml} - xN \\ \hline x = \frac{0.01879}{0.19069} = 0.0985N \end{array}$$

Titration is carried out as follows. Pipette 20-25 ml of the borax solution into a conical flask and add one drop of methyl orange indicator. Add the acid solution from a burette, stirring constantly, until the solution assumes a faint pink colour. During titration set the flask on a glass plate under which a sheet of white paper is placed. It is recommended that titration be conducted with a reference solution (see Sec. 138).

To check the end-point of titration, add to the titrated solution one drop of standard alkali solution. The faint pink colour should change to pale yellow.

Titration is repeated three times. The results of the titrations should differ from each other by not more than 0.1 ml. The test results should be tabulated in the laboratory notebook as follows:

$Na_2B_4O_7 \cdot 10H_2O$ solution taken for titration, ml	Acid solution used in the titration, ml
25.0	23.41
25.0	23.41
25.0	23.48
Mean value 25.0	Mean value 23.43

The normality of the acid solutions is calculated from the mean value of three determinations by the following formula:

$$\frac{V_{acid}}{V_{borax}} = \frac{N_{borax}}{N_{acid}}; \qquad N_{acid} = \frac{N_{borax} \cdot V_{borax}}{V_{acid}}$$

Substituting the data obtained in the above example into the last equation, we have

$$N_{acid} = \frac{0.0985 \times 25.0}{23.43} = 0.105N$$

The titre of the solution and correction K can be determined from the normality. For example:

$$T_{0.105N\ HCl} = \frac{36.46 \times 0.105}{1000} = 0.03828\ \text{g/ml}$$

$$K = \frac{0.105}{0.1} = 1.050$$

Standardization of the acid against separate weighed portions of borax. This method takes a long time, but is more exact because it avoids error always present in measurement of volume by means of the graduated flask and pipette. Each weighed portion should be approximately equivalent to 20-25 ml of solution titrated with the acid.

Procedure. Weigh out on an analytical balance the required amount of chemically pure $Na_2B_4O_7 \cdot 10H_2O$. Transfer the weighed portion accurately to a conical flask, dissolve in water, add one drop of methyl orange indicator and titrate with the acid solution being standardized until a persistent faint pink colour appears.

Example 2. Determine the normality of the HCl solution by means of separate weighed portions of borax.

Calculate the weighed portion of borax. $E_{Na_2B_4O_7 \cdot 10H_2O} = 190.69$. Hence, the amount of $Na_2B_4O_7 \cdot 10H_2O$ (chemically pure) equivalent to 20 ml of $0.1N$ HCl solution is equal to $\frac{190.69 \times 20}{10 \times 1000} = 0.3814$ g; the amount of chemically pure $Na_2B_4O_7 \cdot 10H_2O$ equivalent to 25 ml of the same solution is equal to $\frac{190.69 \times 25}{10 \times 1000} = 0.4767$ g.

Weigh out accurately on an analytical balance two portions of borax weighing approximately 0.4-0.5 g; suppose the actual weights are 0.4248 and 0.4654 g. Dissolve each of the weighed portions in separate conical flasks and titrate with the HCl solution being standardized in the presence of one drop of methyl orange indicator.

Suppose that 22.30 ml of solution were used to titrate the first weighed portion, and 24.50 ml to titrate the second weighed portion. Calculate the results for each titration.

1. The portion of borax weighing 0.4248 *g* is equivalent to $\frac{0.4248}{190.69} = 0.002227$ g-equiv of $Na_2B_4O_7 \cdot 10H_2O$. Hence, 22.3 ml of acid also contain 0.002227 g-equiv of acid.

Therefore, the normality of HCl is equal to

$$N_{HCl} = \frac{0.002227 \times 1000}{22.3} = 0.0999N$$

2. The portion of borax weighing 0.4654 g is equivalent to $\frac{0.4654}{190.69} = 0.002441$ g-equiv of borax. Therefore, the normality of the HCl is equal to

$$N_{HCl} = \frac{0.002441 \times 1000}{24.5} = 0.0996N$$

The mean value of the normality is $0.0998N$

156. Standardization of Hydrochloric Acid Against Sodium Carbonate

The reaction, in this case, proceeds according to the equation

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3$$

It follows that the equivalent weight of Na_2CO_3 is equal to half its molecular mass:

$$M_{Na_2CO_3} = 106; \qquad E_{Na_2CO_3} = \frac{106}{2} = 53$$

On titrating sodium carbonate with hydrochloric acid, sodium chloride and carbonic acid are formed at the equivalence point. The concentration of hydrogen ions in $0.1N$ carbonic acid (considering only the first stage of dissociation) is equal to

$$[H^+] = \sqrt{K'_{H_2CO_3} \cdot C_{H_2CO_3}} = \sqrt{4.3 \cdot 10^{-7} \times 0.1} = \sqrt{4.3 \cdot 10^{-8}} =$$

$$= 2.07 \cdot 10^{-4}$$

and

$$pH = 4 - \log 2.07 = 4 - 0.32 = 3.68$$

Therefore, the indicator used should have a pT-value equal to 4. Methyl orange is such an indicator.

To prepare a 0.1*N* solution of sodium carbonate, it is necessary to dissolve 5.3 g of Na_2CO_3 in one litre of solution. To prepare 200 ml of 0.1*N* solution (the volume of the graduated flask), 5.3 : 5 = 1.06 g of Na_2CO_3 are weighed.

Procedure. Weigh out on an analytical balance approximately 1-1.3 g of chemically pure anhydrous sodium carbonate in a small beaker or on a watch glass. Transfer the weighed portion through a funnel to a graduated flask, dissolve it in water, and make up to the mark. Stopper the flask tightly and mix the solution thoroughly. Calculate the normality from the mass of the weighed portion (see Sec. 155, Example 1).

Example. Suppose that 200 ml of solution were prepared from 1.2280 g of Na_2CO_3. The titre of the solution equals $\frac{1.2280}{200} = 0.00614$ g/ml. The titre of a 1*N* solution is 0.053 g/ml. Hence, we may write the following proportion:

$$\begin{array}{r} 0.053 \quad \text{g/ml}—1N \\ 0.00614 \ \text{g/ml}—xN \\ \hline x = \dfrac{0.00614}{0.053} = 0.116N \end{array}$$

Pipette a definite amount of the prepared sodium carbonate solution into a conical flask. Add one drop of methyl orange indicator and titrate with the hydrochloric acid solution to be standardized from a burette until a persistent pink colour appears. Make at least three titrations and take the mean value of three test results to determine the normality (see Sec. 155, titration of borax with hydrochloric acid).

Find the normality of the acid from the titration results and the normality of the sodium carbonate solution:

$$V_{acid} \cdot N_{acid} = V_{Na_2CO_3} \cdot N_{Na_2CO_3}$$

157. Standardization of an Alkali Against Oxalic Acid

The normality of an alkali solution can be determined against chemically pure $H_2C_2O_4 \cdot 2H_2O$ (COOH—COOH), oxalic acid, or $H_2C_4H_4O_4$(HOOC — CH_2 — CH_2— COOH), succinic acid.

Both are dibasic acids and, consequently, their gram-equivalent is equal to 0.5 mole.

$$E_{H_2C_2O_4 \cdot 2H_2O} = \frac{126.06}{2} = 63.03 \text{ g}$$

$$E_{H_6C_4O_4} = \frac{118.08}{2} = 59.04 \text{ g}$$

To prepare 1 litre of 0.1*N* solution of oxalic acid, 6.303 g of acid are needed per 1 litre of solution. To prepare 200 ml of 0.1*N* solution (the volume of the graduated flask), 6.303 : : 5 = 1.2606 g of oxalic acid are required.

Procedure. Weigh out 1-1.5 g of $H_2C_2O_4 \cdot 2H_2O$ (chemically pure) in a small beaker or on a watch glass to the nearest 0.0002 g on an analytical balance. Transfer the weighed portion through a funnel to a graduated flask, add distilled water to the mark. Tightly stopper the flask and mix thoroughly. Find the normality from the mass of the weighed portion.

Example. Suppose that 200.0 ml of solution were prepared from 1.3240 g of $H_2C_2O_4 \cdot 2H_2O$.

The titre of the prepared solution is equal to $\frac{1.3240}{200} =$ = 0.00662 g/ml; the titre of a 1*N* solutions is 0.06303 g/ml. Hence, we may write the following proportion:

$$\begin{array}{c} 0.06303 \text{ g/ml} — 1N \\ 0.00662 \text{ g/ml} — xN \\ \hline x = \frac{0.00662}{0.06303} = 0.105\text{N} \end{array}$$

Pipette a fixed volume of the oxalic acid solution into a conical flask and add 2 or 3 drops of phenolphthalein indicator. Titrate with the alkali solution to be standardized as described for titration of borax with hydrochloric acid (see Sec. 155). Calculate the normality and titre of the alkali solution being standardized from the test results, using the following formulas:

$$\frac{V_{alkali}}{V_{H_2C_2O_4}} = \frac{N_{H_2C_2O_4}}{N_{alkali}}; \qquad T_{alkali} = \frac{E_{alkali} \cdot N_{alkali}}{1000}$$

Problems

1. Suppose that 200 ml of solution contain 2.000 g of chemically pure $H_2C_2O_4 \cdot 2H_2O$ and 15.00 ml of NaOH solution were used to titrate 20.00 ml of this solution. Find the normality of the NaOH solution.
Ans. 0.212*N*

2. Suppose that 40.00 ml of H_2SO_4 were used to neutralize a solution containing 0.2000 g of chemically pure Na_2CO_3. Determine the normality of the H_2SO_4 solution.
Ans. 0.094*N*

158. Standardization of an Alkali Against a Standard Acid Solution

Pour a fixed volume of a standard acid solution (20.00-25.00 ml) from a burette into a conical flask, add one drop of methyl orange indicator and titrate the acid with the alkali solution to be standardized until a persistent yellow colour appears.

Determine the normality of the alkali from the results of titration and the known normality of the HCl solution.

159. Determination of Sulphuric Acid in the Commercial Product

Procedure. Calculate the mass of 100 per cent H_2SO_4 required to prepare a solution with a concentration approximately equal to that of the standardized alkali solution. Determine the density of the acid under test with the aid of an areometer, find the percentage (approximate) of H_2SO_4 from the Table given in Appendix 4, and calculate the titre of the solution. Find the volume of the acid needed to prepare a solution of approximately the same concentration as that of the standard alkali solution.

Weigh a weighing bottle together with its cover, pour the calculated volume of acid into it, and reweigh. Transfer the wighed portion through a funnel into a graduated flask, add distilled water to the mark, and mix thoroughly. Titrate a fixed volume of the prepared solution with the standard alkali solution in the presence of methyl orange indicator and calculate the percentage of H_2SO_4 from the results of titration.

Example. Determine the percentage of sulphuric acid in a commercial product of a density of 1.804 g/cm³. The concentration of the standard alkali solutions is approximately 0.1*N*.

Determine the amount of 100 per cent H_2SO_4 needed to prepare 250 ml of 0.1*N* solution.

$$E_{H_2SO_4} = \frac{M_{H_2SO_4}}{2} = \frac{98.08}{2} = 49.04 \text{ g}$$

Hence,

$$m_{weighed\ portion} = \frac{49.04 \times 250}{1000 \times 10} = 1.226 \text{ g of } 100\% \ H_2SO_4$$

From the Table given in Appendix 4 we find that sulphuric acid with a density of 1.804 g/cm³ contains 88 per cent H_2SO_4. Find the titre of the solution from the following proportion:

$$\begin{array}{r} 100 \text{ g} — 88 \text{ g } H_2SO_4 \\ 1.804 \text{ g} — x \text{ g } H_2SO_4 \\ \hline x = \frac{88 \times 1.804}{100} = 1.5858 \text{ g } H_2SO_4 \end{array}$$

Therefore, the required volume of acid is equal to $\frac{1.226}{1.5858} =$ $= 0.77$ ml, i.e., about 0.8 ml of acid of the given concentration is needed to prepare an approximately 0.1*N* solution.

Weigh accurately (to the nearest 0.0002 g), in a closed weighing bottle, 1 ml of the acid under analysis (1.3146 g) and prepare 250 ml of solutions. Suppose 25.78 ml (the mean value) of 0.101*N* NaOH solution were used to titrate 25.00 ml of the prepared solution.

The titre of the standard solution of NaOH in terms of H_2SO_4 is

$$T_{NaOH/H_2SO_4} = \frac{E_{H_2SO_4} \cdot N_{NaOH}}{1000} = \frac{49.04 \times 0.101}{1000} = 0.004953 \text{ g/ml}$$

This is the amount of H_2SO_4 titrated with 1 ml of NaOH. Since 25.78 ml were used to titrate 25.00 ml of H_2SO_4, the content of H_2SO_4 in 25.00 ml is 0.004953×25.78, and in the weighed portion (in the volume of the graduated flask) it is $\frac{0.004953 \times 25.78 \times 250}{25} = 1.277$ g of H_2SO_4. The weig-

hed portion, therefore, contains $\frac{1.277 \times 100}{1.3146} = 97.1$ per cent of H_2SO_4.

The same results can be obtained by calculating the normality of the sulphuric acid:

$$\frac{N_{H_2SO_4}}{0.101} = \frac{25.78}{25}; \qquad N_{H_2SO_4} = \frac{0.101 \times 25.78}{25} = 0.104N$$

The weighed portion contains $\frac{49.04 \times 0.104 \times 250}{1000} =$ $= 1.275$ g of H_2SO_4 or $\frac{1.275 \times 100}{1.3146} = 97.0$ per cent of H_2SO_4.

The percentage of CH_3COOH in the commercial product is determined in the same way as H_2SO_4, the only difference being that phenolphthalein is used as the indicator when titrating with the alkali solution.

Questions and Problems

1. What standard solutions and indicators are used in acid-base titrations?
2. How are acid and alkali solutions prepared and standardized?
3. How is the normality of a solution of alkali hydroxide determined?
4. Why is chemically pure borax used as a primary standard for determining the normality of standard acid solutions?
5. How is the molarity of a solution determined from its concentration in per cent and its density?
6. Suppose 200.0 ml of solution were prepared from 1.050 g of $H_2C_2O_4 \cdot 2H_2O$ and 15.00 ml of $0.1N$ NaOH were used to titrate 20.00 ml of the prepared solution. Determine the percentage of $H_2C_2O_4 \cdot 2H_2O$ in the sample under test.

Ans. 90.04 per cent

7. A sample of marble weighing 2.500 g was dissolved in 50.00 ml of $1N$ HCl and 30.00 ml of $0.1N$ NaOH were used to titrate the excess of acid. Determine the percentage of $CaCO_3$ in the sample under test.

Ans. 94.08 per cent

160. Determination of the Respective Amounts of Alkali and Alkali Carbonate Present Together in Solution

The respective contents of alkalies and carbonates of alkali metals in solution are determined in two ways.

Method 1. Solid alkali and its solution are always contaminated with carbonate unless they are specially freed

from carbonates. When titrating an alkali solution containing carbonate, the acid reacts with the alkali and the carbonate. Two reactions take place:

$$NaOH + Na_2CO_3 + 2HCl = 2NaCl + NaHCO_3 + H_2O \quad (1)$$

$$NaHCO_3 + HCl = NaCl + H_2CO_3 \quad (2)$$

At the end of the first reaction, the solution contains in addition to NaCl (which does not affect the concentration of H^+ ions) $NaHCO_3$. Due to hydrolysis of the latter, the pH of the solution is equal to 8.38. At this point, as seen from equation (1), the acid neutralizes all of the alkali, and all of the carbonate is converted to the bicarbonate. At the end of reaction (2) the bicarbonate is neutralized and H_2CO_3 is formed. Therefore, at the end of titration the pH of the solution is equal to 3.77.

Let us see what takes place on titrating the solution in the presence of phenolphthalein indicator and what occurs in the presence of methyl orange indicator. At the beginning of titration when the solution contains alkali and alkali carbonate (the pH of the solution is greater than 10), the addition of phenolphthalein indicator imparts a red-violet colour to the solution; and methyl orange indicator, a yellow colour. Phenolphthalein is decolourized at the moment when all the alkali is neutralized and the carbonate is converted to bicarbonate (pH = 8.38). The yellow colour of the solution in the presence of methyl orange indicator will turn pink when all the alkali is neutralized and the carbonate is converted to carbonic acid (pH = 3.77).

By determining the volume of acid used to neutralize the alkali and the volume of acid used to neutralize the carbonate, it is a simple matter to obtain the respective amounts in per cent of the alkali and carbonate in the sample.

Procedure. When calculating the weighed portion of the sample, only the content of alkali (contaminated with carbonate) is taken into account. Weigh out the portion in a weighing bottle, dissolve it in distilled water which has been previously boiled and cooled (to remove CO_2). Transfer the solution to a graduated flask, make up to the mark with water, and mix thoroughly. Pipette a fixed volume of the resulting solution into a conical flask. Add 2 or 3 drops of phenolphthalein indicator and titrate with a standard acid solution

until the pink colour disappears. Record the volume of acid used in the laboratory notebook.

Then add to the solution being titrated 1 or 2 drops of methyl orange indicator and titrate until a persistent faint pink colour appears. Record the volume of acid used in the notebook.

Example. A sample of NaOH is contaminated with Na_2CO_3. Calculate the weighed portion g required to prepare a solution in a 250-ml graduated flask:

$$g = \frac{E_{NaOH} \times N_{NaOH} \times 250}{1000} = \frac{40.0 \times 0.1 \times 250}{1000} = 1 \text{ g}$$

Suppose that 250 ml of solution were prepared from a weighed portion of 0.9546 g, and for the titration of 25 ml of this solution the quantity of 0.0995N HCl used was: 19.60 ml in the presence of phenolphthalein indicator and 20.70 ml in the presence of methyl orange indicator. Then, 20.70 — — 19.60 = 1.10 ml of HCl were used to convert Na_2CO_3 to $NaHCO_3$ and 1.10 × 2 = 2.20 ml of HCl were used to convert the bicarbonate to carbonic acid. The amount used to titrate NaOH was, therefore, 20.70 — 2.20 = 18.50 ml of HCl.

The titre of the standard HCl solution in terms of Na_2CO_3 is

$$T_{0.0995N\ HCl/Na_2CO_3} = \frac{53.00 \times 0.0995}{1000} = 0.00527 \text{ g/ml}$$

The titre of the HCl solution in terms of NaOH is

$$T_{0.0995N\ HCl/NaOH} = \frac{40.00 \times 0.0995}{1000} = 0.00398 \text{ g/ml}$$

Hence, 25.00 ml of the solution contain:

$$0.00527 \times 2.20 = 0.01159 \text{ g } Na_2CO_3$$
$$0.00398 \times 18.50 = 0.07363 \text{ g NaOH}$$

and 250 ml of solution contain:

$$\frac{0.01159 \times 250}{25} = 0.1159 \text{ g } Na_2CO_3 \text{ or } \frac{0.1159 \times 100}{0.9546} =$$
$$= 12.14\% \ Na_2CO_3$$
$$\frac{0.07363 \times 250}{25} = 0.7363 \text{ g NaOH or } \frac{0.7363 \times 100}{0.9546} =$$
$$= 77.13\% \text{ NaOH}$$

Method 2. Titrate the solution containing alkali and carbonate with standard acid solution in the presence of methyl orange indicator to determine the volume of acid equivalent to the total alkalinity of the solution due to the presence of alkali and carbonate. To another equal volume of the solution under test add a small excess of $BaCl_2$ in order to precipitate CO_3^{2-} ions. Titrate the alkali hydroxide remaining in the solution in the presence of phenolphthalein indicator. The difference between the amounts of acid used in the two titrations is equivalent to the amount of carbonate contained in solution.

Procedure. Calculate the weighed portion, as in the previous case, taking into account only the alkali. Prepare from the weighed portion a solution in a graduated flask. Pipette a fixed volume of the resulting solution into a conical flask and titrate it with the standard acid solution in the presence of methyl orange indicator. To another equal volume of solution add 10 ml of 10 per cent $BaCl_2$ solution and, without filtering, titrate with the same standard acid solution in the presence of phenolphthalein indicator.

Calculations are made in the same way as in the first method.

161. Determination of Ammonia in Aqueous Solutions

A weighed portion of the solution under test is diluted with water so that its normality is approximately equal to that of the standard acid solution and the determination is carried out by the method used for determining the content of H_2SO_4 (see Sec. 159).

Procedure. First determine with an areometer the density of the solution under test and find the approximate percentage of NH_3 from the Table in Appendix 4. Weigh accurately in a closed weighing bottle an amount of the solution under test approximately equal to the calculated weighed portion. Transfer to a graduated flask, make up to the mark with water, and mix thoroughly.

Since ammonia is volatile and there may be losses if direct titration is used, it is recommended that back titration be employed for the determination. To a fixed volume of stan-

dard acid solution (taken in excess) add by means of a pipette a fixed volume of the solution under test, and titrate the excess of acid with standard alkali solution. Simultaneously, titrate with the standard alkali solution the same amount of acid as was added to the test solution. Calculate the amount of ammonia in the sample under test by the difference between the volume used for titrating all the acid solution added and the volume used for titrating the excess of acid after neutralizing the ammonia.

The titre of the alkali solution in terms of ammonia is

$$T_{NaOH/NH_3} = \frac{17.03 \cdot N_{NaOH}}{1000}$$

The mass of NH_3 in the volume of the sample is

$$m_{NH_3} = \frac{17.03 \cdot N_{NaOH}}{1000} (V_1 - V_2)$$

where V_1 = volume of alkali used for titrating all the acid added;

V_2 = volume of alkali used for titrating the excess of acid.

Consequently, the percentage of ammonia in the solution is equal to

$$\frac{17.03 \cdot N_{NaOH} \cdot (V_1 - V_2) \cdot V_{flask} \cdot 100}{1000 \cdot V_{sample} \cdot \text{weighed portion}}$$

Questions and Problems

1. How are the respective amounts of alkali and carbonate determined when both are present in a solution?

2. What volume of 0.1*N* HCl is needed to neutralize a solution containing 0.265 g of Na_2CO_3: (a) in the presence of phenolphthalein indicator and (b) in the presence of methyl orange indicator?

Ans. (a) 25.0 ml; (b) 50.0 ml

3. Suppose that 250 ml of solution were prepared from 6 g of the sample under test. To neutralize 25 ml of the resulting solution, 18 ml of 0.5*N* hydrochloric acid were used in the presence of phenolphthalein indicator, and 25 ml of the same acid in the presence of methyl orange indicator. Determine the percentage of NaOH and Na_2CO_3.

Ans. 36.67 per cent of NaOH and 61.83 per cent of Na_2CO_3

162. Determination of Hardness of Water

Hardness of water is determined by the content in it of soluble magnesium and calcium salts, i.e., the bicarbonates, sulphates, and chlorides of magnesium and calcium. There are two types of hardness: carbonate (temporary) and non-carbonate (permanent) hardness.

Temporary hardness is due to the presence of the soluble bicarbonates $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. On boiling the water, the bicarbonates are converted to the insoluble carbonates:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2$$

Temporary hard water is almost completely softened by boiling. Temporary hardness is denoted as H_t.

Permanent hardness of water is due to the presence of sulphates and chlorides of calcium and magnesium that remain in solution on boiling the water. Permanent hardness is denoted as H_p. Usually, the total hardness H_T and temporary hardness H_t are determined and the permanent hardness H_p is determined by the difference between H_T and H_t.

In the Soviet Union the unit of hardness is 1 mg-equiv of magnesium and calcium salts contained in 1 litre of water. Thus, the hardness of water is equal to 5 mg-equiv if it contains in 1 litre 5 mg-equiv of magnesium and calcium salts.

Temporary hardness of water is determined as described below.[1]

Procedure. Rinse a 100-ml graduated flask two or three times with the water under test and then fill it with this water to the mark. Transfer all the water quantitatively to a conical flask, add 1 or 2 drops of methyl orange indicator, and titrate with standard HCl solution until a persistent faint pink colour appears. The acid neutralizes only the bicarbonates of calcium and magnesium:

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2H_2O + 2CO_2$$

$$Mg(HCO_3)_2 + 2HCl = MgCl_2 + 2H_2O + 2CO_2$$

[1] Total hardness is determined by complexometric titration (see Sec. 194).

The amount of acid used in the titration is equivalent to the amount of calcium and magnesium bicarbonates in the water being titrated.

Since the normality of a solution is the number of gram-equivalents of solute in 1 litre or the number of milligram-equivalents in 1 ml, the product of the normality of the hydrochloric acid and the number of millilitres used in the titration is equal to the number of milligram-equivalents of the bicarbonates contained in 100 ml of water. Temporary hardness is determined by multiplying the product obtained by 10.

Temporary hardness can be calculated from the following formula:

$$H_t = V_{HCl} \cdot N_{HCl} \cdot 10$$

Example. Suppose that 3.4 ml of 0.0988*N* HCl solution were used to titrate 100 ml of water under test with methyl orange as indicator.

Then,

$$H_t = 3.4 \times 0.0988 \times 10 = 3.36 \text{ mg-equiv/lit}$$

On titrating 100 ml of water with an exactly 0.1*N* acid solution (prepared, for example, from a primary standard), the hardness of the water is equal to the number of millilitres of the acid used in the titration.

CHAPTER XXXVI

Oxidation-Reduction Titrations—I Permanganate Method

163. General Principles of Oxidimetric Titrations

In oxidimetric titrations use is made of oxidation-reduction reactions which always involve the transfer of electrons from one element or ion to another.

The value of the gram-equivalent of oxidizing and reducing agents in oxidation-reduction reactions is taken as the number of grams of substance equivalent to one electron ga-

ined or lost by one molecule of the substance in a given reaction.

The gram-equivalent of an oxidizing or reducing agent is expressed by the formula

$$E = \frac{M}{n}$$

where

E = gram-equivalent;
M = molecular mass of oxidizing (reducing) agent;
n = number of electrons gained (lost) by the elements or ions of each molecule of oxidizing (reducing) agent.

To determine n it is necessary to know the original and final valency of the oxidizing or reducing agent. The gram-equivalent of an oxidizing (reducing) agent is equal to the quotient obtained on dividing the gram-molecule by n corresponding to the change in valency of the elements or ions constituting the molecule of the oxidizing (reducing) agent.

164. Principles of the Permanganate Method

Titrations involving permanganate oxidation is a special case of oxidimetry in which a solution of potassium permanganate, $KMnO_4$, is used as the oxidant. The ability of $KMnO_4$ solution to oxidize is due to the conversion of the MnO_4^- ion to Mn^{2+} in acidic solution and to MnO_2 in alkaline, neutral, or very feebly acidic solution. The MnO_4^- ion is reduced in accordance with the following reactions:

In acidic solution

$$MnO_4^- \rightarrow Mn^{2+}; \quad MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$

Hence,

$$E_{KMnO_4} = \frac{M_{KMnO_4}}{5}$$

In alkaline, neutral, or very feebly acidic solution

$$MnO_4^- \rightarrow MnO_2; \quad MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$$

In this reaction,

$$E_{KMnO_4} = \frac{M_{KMnO_4}}{3}$$

Solutions containing MnO_4^- ions are purple in colour, solutions of salts containing Mn^{2+} ions are colourless. Therefore, a permanganate solution is decolourized when added to a solution of a reducing agent as long as the latter is present in the solution. The moment there is an excess of $KMnO_4$, the solution becomes purple. Thus, the permanganate ion can serve as its own indicator, especially in acidic solutions. In neutral and alkaline solutions, however, (because of the formation of brown particles of MnO_2) diphenylamine or phenylanthranilic acid is used as indicator with very dilute solutions of potassium permanganate (0.001*N*).

Potassium permanganate solution is used in determination of both reducing and oxidizing agents—the former by direct titration, the latter by back titration. In back titration, to a known (measured) volume of the oxiding agent is added a suitable reductant taken in excess. The excess of reductant is titrated with standard permanganate solution. The concentration of the added solution of the reductant is determined separately by titrating with the same standard permanganate solution.

165. Preparation of Potassium Permanganate Solution

Since titration with potassium permanganate is mainly conducted in acidic solution, the weighed portion of $KMnO_4$ required to prepare the standard solution is calculated as follows:

$$E_{KMnO_4} = \frac{M_{KMnO_4}}{5} = \frac{158.03}{5} = 31.61 \text{ g}$$

To prepare 1 litre of 0.1*N* solution weigh out approximately 3.2 g of $KMnO_4$ on a rough balance; dissolve the weighed portion in hot water; dilute with cold water to a volume of 1 litre and mix thoroughly. The freshly prepared solution is allowed to settle. The precipitate in the solution is usually MnO_2 which is often present in the potassium permanganate used. Besides, distilled water may contain some reducing agents in the form of organic compounds which partly reduce the $KMnO_4$ to MnO_2. Therefore, the titre of the $KMnO_4$ solution is determined only 7-10 days after its preparation. The solution is then filtered through glass

wool[1]; the $KMnO_4$ solution is kept in a dark glass bottle.

The $KMnO_4$ should by no means come in contact with rubber tubing, therefore, titration with potassium permanganate solution is conducted in burettes with glass stopcocks. Solutions of $KMnO_4$ should not be kept for long periods of time in burettes or other glassware because a brown film of MnO_2 is formed on the surface of the glass. This film can be washed off with concentrated HCl solution, a mixture of $2N$ sulphuric acid solution and ferrous ammonium sulphate solution, or with oxalic acid.

166. Standardization of Potassium Permanganate Solution

The standardization of potassium permanganate solution against chemically pure oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, is based on the following reaction:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + \\ + 10CO_2 + 8H_2O$$

$$2 \mid MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$
$$5 \mid C_2O_4^{2-} - 2e = 2CO_2$$

It is evident from the equation that when the $C_2O_4^{2-}$ ion is oxidized to CO_2, it gives away two electrons and the gram-equivalent of $H_2C_2O_4$ is therefore equal to 0.5 mole:

$$E_{H_2C_2O_4 \cdot 2H_2O} = \frac{M_{H_2C_2O_4 \cdot 2H_2O}}{2} = \frac{126.07}{2} = 63.03 \text{ g}$$

A disadvantage of oxalic acid is that it is efflorescent and gradually loses its hydration (crystal) water on standing; therefore, it is necessary to recrystallize it. It is better to use sodium oxalate, $Na_2C_2O_4$, which, in contrast to oxalic acid, crystallizes without water and is not hygroscopic. The equation for the reaction between $KMnO_4$ and $Na_2C_2O_4$ is

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + \\ + 10CO_2 + 5Na_2SO_4 + 8H_2O$$

[1] The permanganate solution can be filtered through a sintered glass filter with suction.

Hence,

$$E_{Na_2C_2O_4} = \frac{M_{Na_2C_2O_4}}{2} = \frac{134.01}{2} = 67.01 \text{ g}$$

Procedure. Weigh out the portion of $Na_2C_2O_4$ or $H_2C_2O_4 \cdot 2H_2O$ required to prepare a solution of approximately the same normality as the $KMnO_4$ solution being standardized. In a conical flask heat approximately 30 ml of $2N$ H_2SO_4 solution almost to the boiling point. Pipette a fixed volume of the $Na_2C_2O_4$ or $H_2C_2O_4$ solution into the hot solution and then titrate the resulting solution with the $KMnO_4$ solution. Add the first 1-2 ml of $KMnO_4$ drop by drop (adding each consecutive drop only after the preceding drop is decolourized) and shake the flask vigorously. As the reaction proceeds, decolouration is accelerated due to the formation of Mn^{2+} ions which act as a catalyzer in this reaction.

Titration with permanganate solution should be continued until a pink colour due to one excess drop of $KMnO_4$ appears and persists for a minute (or a longer period of time).

The solution being titrated with oxalic acid or sodium oxalate must be hot. If towards the end of titration it gets cold, it should be reheated without bringing it, however, to the boiling point. If the titrated solution turns brown instead of pink, some mistake has been made in titrating, and the test should be repeated.

Example. To prepare 200.0 ml of $0.1N$ sodium oxalate solution, it is necessary to dissolve 1.3402 g of chemically pure $Na_2C_2O_4$; suppose the weighed portion actually dissolved was 1.4380 g and the mean value of $KMnO_4$ used to titrate 25.00 ml of the resulting solution was 23.85 ml.

1. Determine the normality of the $Na_2C_2O_4$ solution prepared. The titre of $1N$ $Na_2C_2O_4$ solution is 0.06701 g/ml. The titre of the solution prepared is $\frac{1.4380}{200} = 0.00719$ g/ml. The normality of the solution prepared is found from the following proportion:

$$\begin{array}{l} 0.0670 \text{ g/ml} — 1N \\ 0.00719 \text{ g/ml} — xN \\ \hline x = \dfrac{0.00719}{0.06701} = 0.1073N \end{array}$$

2. Determine the normality of the permanganate solution from the results of titration:

$$V_{KMnO_4} \cdot N_{KMnO_4} = V_{Na_2C_2O_4} \cdot N_{Na_2C_2O_4}$$

Hence,

$$N_{KMnO_4} = \frac{V_{Na_2C_2O_4} \cdot N_{Na_2C_2O_4}}{V_{KMnO_4}} = \frac{25 \times 0.1073}{23.85} = 0.112N$$

The titre of the $KMnO_4$ solution is

$$T_{KMnO_4} = \frac{31.61 \times 0.112}{1000} = 0.003540 \text{ g/ml}$$

The titre of the same permanganate solution in terms of iron is

$$T_{KMnO_4/Fe} = \frac{55.85 \times 0.112}{1000} = 0.006255 \text{ g/ml}$$

167. Determination of Iron (II)

Ferrous ions, Fe^{2+}, are readily oxidized by potassium permanganate in acidic solution. Titration with potassium permanganate is one of the most important methods for the quantitative determination of iron.

Let us determine the content of iron in a solution of ferrous ammonium sulphate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt).

The reaction between $KMnO_4$ and Mohr's salt in acidic solution proceeds as follows:

$$10(NH_4)_2Fe(SO_4)_2 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 10(NH_4)_2SO_4 + 8H_2O$$

$$\begin{array}{r|l|l} 2 & 1 & MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \\ 10 & 5 & Fe^{2+} - e = Fe^{3+} \end{array}$$

Since the Fe^{2+} ion gives away one electron, the gram-equivalent of ferrous ammonium sulphate is equal to the gram-molecule of the salt:

$$E_{(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O} = 392.11 \text{ g}$$

Procedure. Dissolve a weighed portion of ground ferrous ammonium sulphate without heating (to avoid oxidation of Fe^{2+} by atmospheric air). Transfer the resulting solution

to a graduated flask and acidify with 30-40 ml of $2N$ H_2SO_4 solution. Make up to the mark with water. Pipette a fixed volume of the prepared solution into a conical flask, add another 20-30 ml of $2N$ H_2SO_4 solution and titrate in the cold with standard permanganate solution until the solution turns a faint pink colour that persists for 1 minute.

The titre of the permanganate solution in terms of iron (II) can be calculated from its normality:

$$T_{KMnO_4/Fe} = \frac{E_{Fe} \cdot N_{KMnO_4}}{1000} \text{ g/ml}$$

The amount of iron (II) in the weighed portion and the percentage in the sample under test can be calculated from the results of titration.

Example. Suppose that 21.20 ml of $0.113N$ solution of $KMnO_4$ were used to titrate 25.00 ml of Mohr's salt.

The titre of $KMnO_4$ in terms of iron is

$$T_{KMnO_4/Fe} = \frac{55.85 \times 0.113}{1000} = 0.006311 \text{ g/ml}$$

The mass of iron in the pipetted volume is

$$0.006311 \times 21.20 = 0.1338 \text{ g}$$

Calculate the amount of iron in the weighed portion, taking into account the volume of the graduated flask in which it was dissolved. Determine the amount of iron in per cent of the weighed portion.

168. Determination of Chromium in Potassium Dichromate

Potassium permanganate being an oxidant does not react directly with other oxidizing agents. Therefore, the percentage of oxidizing agents is determined with permanganate solution by back titration, i.e., a reductant is added in excess to a definite volume of the oxidizing agent and then the excess of reductant is titrated with standard potassium permanganate solution. The concentration of the reductant is determined by direct titration with the same permanganate solution. When determining the chromium content in potassium dichromate, it is convenient to use a ferrous salt as

the reductant; it reacts with $K_2Cr_2O_7$ according to the equation

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$$1 \mid Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$$

$$6 \mid Fe^{2+} - e = Fe^{3+}$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Since chromium in the $Cr_2O_7^{2-}$ ion takes on 6 electrons, the gram-equivalent of $K_2Cr_2O_7$ is equal to $^1/_6$ mole.

Procedure. Calculate the weighed portion of $K_2Cr_2O_7$ needed to obtain a solution of a normality approximately equal to that of the standard $KMnO_4$ solution.

Dissolve the weighed portion in water, transfer the solution to a graduated flask, make up to the mark with water, and mix well. Pipette a fixed volume of the $K_2Cr_2O_7$ solution into a conical flask, add 30-40 ml of $2N$ H_2SO_4 solution and 40.00-50.00 ml of Mohr's salt. Titrate the excess of Mohr's salt with the standard potassium permanganate solution until the solution becomes grey. This colour is produced by the combination of the green colour of the Cr^{3+} ion and the pink colour of the MnO_4^- ion. Simultaneously, titrate the same amount of Mohr's salt (as was previously added to the dichromate solution) in the presence of 30-40 ml of $2N$ H_2SO_4 solution.

Determine the equivalent amount of potassium dichromate contained in the titrated sample of the solution under test by the difference between the volume of the potassium permanganate solution used in the titration of the Mohr's salt added and the volume used in the titration of the excess of Mohr's salt remaining after the reaction of the salt with $K_2Cr_2O_7$.

The titre of the permanganate solution in terms of chromium is calculated from the formula

$$T_{KMnO_4/Cr} = \frac{E_{Cr} \cdot N_{KMnO_4}}{1000}$$

The gram-equivalent of chromium is equal to $\frac{\text{g-atom}}{3}$:

$$E_{Cr} = \frac{1 \text{ g-atom Cr}}{3} = \frac{52.00}{3} = 17.33 \text{ g}$$

The number of grams of chromium in the pipetted volume is

$$\frac{17.33 \cdot N_{KMnO_4} \cdot (V_1 - V_2)}{1000}$$

where V_1 = volume of standard permanganate solution used in the titration of the total volume of Mohr's salt;

V_2 = volume of the same permanganate solution used in the titration of the excess of Mohr's salt.

If we know the weighed portion of $K_2Cr_2O_7$, the volume of the solution prepared, and the capacity of the pipette used, we can calculate the percentage of chromium in the sample under test.

Questions and Problems

1. What standard solution and indicator are used in the permanganate method?
2. In what determinations is titration with potassium permanganate used?
3. How are reducing and oxidizing agents analyzed by titration with potassium permanganate?
4. How is the gram-equivalent of an oxidizing or reducing agent determined?
5. What is the gram-equivalent of each of the following oxidizing and reducing agents: Cl_2, $KClO_3$, K_2SO_3, H_2O_2, and $KMnO_4$ in acidic and alkaline solutions?
6. Against what chemically pure substance is the normality of $KMnO_4$ solution usually determined?
7. Write the equation for the reaction between $Na_2C_2O_4$ and $KMnO_4$ in acidic solution.
8. A litre of solution contains 0.3161 g $KMnO_4$. Determine the normality of this solution and its titre in terms of iron.

Ans. 0.010*N*; 0.0005585 g/ml

9. Suppose that 22.5 ml of standard $KMnO_4$ solution were used in the titration of 20.0 ml of solution of $H_2C_2O_4$ containing 5.04 g of $H_2C_2O_4 \cdot 2H_2O$ in 400.0 ml of solution. Determine the normality of the $KMnO_4$ solution and its titre in terms of iron. How much water must be added to 1 litre of the solution to obtain 0.1*N* solution?

Ans. 0.178*N*; 0.00994 g/ml; 780.0 ml of water

10. Suppose 200 ml of solution were prepared from 1.7000 g of commercial crystalline oxalic acid and 16.20 ml of 0.1*N* $KMnO_4$ solution were used to titrate 20.0 ml of the prepared solution. Determine the percentage of $H_2C_2O_4 \cdot 2H_2O$ in the sample under test.

Ans. 60.04 per cent

CHAPTER XXXVII

Oxidation-Reduction Titrations — II Iodometric Method

169. General Principles

The iodometric method of analysis is based on reactions in the course of which free iodine is formed or used.

The reaction for formation of iodine is

$$2I^- - 2e = I_2^0 \qquad (1)$$

The reaction for the reduction of iodine is

$$I_2 + 2e = 2I^- \qquad (2)$$

The formation of free iodine (1) takes place as a result of oxidation of hydriodic acid, HI, with an oxidizing agent. The hydriodic acid is obtained directly in the reaction flask by the action of dilute HCl or H_2SO_4 on a solution of KI:

$$2KI + H_2SO_4 = K_2SO_4 + 2HI$$

Free iodine is liberated as a result of the oxidation of KI in acidic solution:

$$10KI + 2KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

$$\begin{array}{r|c|l} 10 & 5 & I^- - e = I^0 \\ 2 & 1 & MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \end{array}$$

The iodine liberated is titrated with a standard solution of sodium thiosulphate, $Na_2S_2O_3$, which is oxidized to sodium tetrathionate, $Na_2S_4O_6$:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

Free iodine is converted to I^- ion with a reducing agent.

Thus, iodometry is used for the quantitative determination of oxidizing and reducing agents. Standard solutions of sodium thiosulphate and iodine are used in this method with starch as indicator: starch gives with free iodine a blue colour. Due to its great sensitivity, iodometry is the most exact method for determining the percentage of oxidizing and reducing agents.

170. Determination of Oxidizing Agents

Most oxidizing agents cannot be determined by direct titration with sodium thiosulphate because the reaction between the thiosulphate and oxidizing agent is complicated and the end products are indefinite. This makes it impossible to determine the equivalence point. Therefore, displacement titration is used in iodometry. An excess of KI and a solution of H_2SO_4 or HCl are added to the solution of the oxidizing agent. The latter liberates an equivalent amount of iodine which is then titrated with sodium thiosulphate, $Na_2S_2O_3$. The amount of $Na_2S_2O_3$ used to titrate the liberated iodine is equivalent to the amount of oxidizing agent in the solution.

The usual formula can be used for calculation:

$$V_{oxidant} \cdot N_{oxidant} = V_{Na_2S_2O_3} \cdot N_{Na_2S_2O_3}$$

As the oxidation of hydrogen iodide is a reversible reaction:

$$2HI + O \rightleftarrows I_2 + H_2O$$

an excess of KI must be taken for complete evolution of HI. Only on this condition will the oxidizing agent react completely with HI (i.e., with KI in acidic solution). Besides, an excess of KI is needed because it promotes dissolution of the liberated iodine which is only sparingly soluble in water that does not contain KI. Therefore, the amount of KI added should be 3-4 times (but not more than 5 times) the calculated quantity. For each titration, to 20-25 ml of 0.1*N* solution of the oxidizing agent add 15 ml of 10 per cent KI. This quantity is obtained as follows: 20-25 ml of 0.1*N* solution of the oxidizing agent is equivalent to the same volume of 0.1*N* KI which contains $\frac{166.01 \times 0.1 \times 25}{1000} =$ $= 0.4150$ g. Three times this quantity is approximately 1.5 g of KI which is contained in 15 ml of 10 per cent KI. Since the rate of oxidation of iodide ions, I^-, depends on the concentration of hydrogen ions, H^+, as seen from the reaction

$$Cr_2O_7^{2-} + 14H^+ + 6I^- = 2Cr^{3+} + 3I_2 + 7H_2O$$

an excess of acid must be taken. However, 30-40 ml of 2*N* H_2SO_4 or HCl is sufficient for each determination. A greater

excess can affect the results of subsequent titration with sodium thiosulphate which in strongly acidic solution tends to react with the acid:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3$$
$$H_2S_2O_3 = H_2SO_3 + S$$

The resulting H_2SO_3 reacts with iodine:

$$H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4$$

Thus, it can be seen that the gram-equivalent of H_2SO_3 is equal to 0.5 mole, whereas the gram-equivalent of $Na_2S_2O_3$ is equal to 1 mole. Therefore, in the presence of a great excess of a strong acid, the iodine actually reacts with a smaller quantity of $Na_2S_2O_3$ than that required by the reaction equation. To avoid decomposition of sodium thiosulphate, it is necessary, prior to titration, to considerably dilute the solution under test to decrease its acidity.

In iodometric determinations, the starch indicator is added towards the end of titration to prevent intense adsorption of iodine. The iodine adsorbed by the starch passes into solution with difficulty and this can give erroneous test results.

A blue colour sometimes reappears at the end of titrations with very dilute solutions of thiosulphate. This has been explained by the fact that the reaction of the oxidizing agent with KI in acidic solution does not go to an end because of the low concentration of acid or potassium iodide in the solution or too early dilution of the latter with water. Sometimes the reappearance of the blue colour is caused by the oxidation of HI by atmospheric oxygen due to the effect of sunlight.

171. Determination of Reducing Agents

In iodometric determination of reducing agents, the sample under test is titrated with iodine solution and the amount used in the titration is measured directly or by back titration. Since the reaction between the reducing agent and iodine proceeds rather slowly, back titration is usually applied: an excess of standard iodine solution is added to the solution of the reducing agent under test, the mixture is

allowed to stand for some time, and the excess of iodine is titrated with standard sodium thiosulphate solution.

The iodometric method can be used to titrate reducing agents whose oxidation-reduction potentials are less than the potential of conversion of I_2 to $2I^-$ ions (0.54 V). Examples of such reducing agents are thiosulphates, hydrogen sulphide, stannous chloride.

The following conditions must be observed in iodometric titrations:

1. Titrate in the cold, because iodine is volatile and the sensitivity of the reaction of iodine and starch is reduced on raising the temperature.

2. Do not titrate in strongly alkaline solution, because iodine reacts in such conditions not only with the reducing agent but with the alkali as well:

$$I_2 + 2NaOH = NaOI + NaI + H_2O$$

or

$$I_2 \quad 2OH^- = OI^- + I^- + H_2O$$

Therefore, the pH of the solution being titrated should not exceed 9.

3. As the reaction between the solution of the reducing agent under test and iodine proceeds rather slowly, begin to titrate the excess of iodine only when some time has elapsed after adding the iodine.

4. Keep the reacting mixture in the dark, preferably in a flask with a ground-glass stopper, as iodine evaporates readily and sunlight accelerates the side reaction of oxidation of I^- by atmospheric oxygen to free iodine:

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

172. Preparation of Sodium Thiosulphate Solution

Let us study the oxidation-reduction process that takes place when $Na_2S_2O_3$ reacts with I_2:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

sodium tetrathionate

$$1 \mid 2S_2O_3^{2-} - 2e = S_4O_6^{2-}$$
$$1 \mid I_2 + 2e = 2I^-$$

Since two $S_2O_3^{2-}$ ions lose two electrons (each ion loses one electron), the gram-equivalent of sodium thiosulphate is equal to 1 mole:

$$E_{Na_2S_2O_3 \cdot 5H_2O} = M_{Na_2S_2O_3 \cdot 5H_2O} = 248.21 \text{ g}$$

The normality of the sodium thiosulphate solution cannot be determined from the weighed portion used to prepare it because the water of crystallization of the salt is loosely bound and efflorescence may occur. Hence, its composition does not always correspond to the formula $Na_2S_2O_3 \cdot 5H_2O$. A sodium thiosulphate solution of approximate concentration is prepared, which is then standardized against a primary standard (see Sec. 174 and 175).

Procedure. To prepare an approximately 0.1*N* solution of sodium thiosulphate,[1] dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 1 litre of freshly boiled and cooled distilled water. On standing, slow decomposition occurs causing precipitation of sulphur, especially in the presence of sunlight and microorganisms. Such a solution is unsuitable for work. The sodium thiosulphate solution is therefore kept in a dark glass bottle. The bottle is closed with a stopper carrying a guard tube of soda lime and is connected to the burette by means of a siphon (see Fig. 30*a*).

173. Preparation of Starch Solution

In the presence of iodide, starch forms with iodine an intensely coloured blue adsorption complex.

The starch solution is prepared as follows: mix 0.5 g of soluble starch with a small amount of cold water, shaking vigorously; then pour the mixture in a thin stream into 100 ml of boiling water, mix well, and boil for 1-2 minutes. Add 1 g of a preservative (salicylic acid or zinc chloride) to the mixture. After cooling, the solution is ready for use.

Starch decomposes readily in the presence of various microorganisms; it is recommended therefore that it be kept in a flask stoppered with cotton wool. A preservative is added to the starch solution for the same reason.

[1] Very dilute solutions, for example, 0.05 or 0.01*N* solutions can also be used.

The starch solution should be homogeneous, without any lumps, because the iodine adsorbed by the latter is extracted by water with difficulty. If the solution is prepared properly it should give an intense blue colour with 2 or 3 drops of 0.01*N* iodine solution. A reddish-brown colour indicates decomposition of the starch solution which is no longer suitable for use.

In each titration, 2-3 ml of starch solution is added to the solution being titrated.

174. Standardization of Sodium Thiosulphate Solution Against Chemically Pure Potassium Dichromate

The thiosulphate solution is standardized against chemically pure iodine or one of the following oxidizing agents: $K_2Cr_2O_7$, $KMnO_4$, KIO_3, HIO_3. Iodine is rarely used for this purpose.

To obtain chemically pure $K_2Cr_2O_7$, the pure reagent is recrystallized twice from hot aqueous solution. The crystals formed are previously ground and then dried in a drying chamber at 150-200°C.

Thiosulphate is not used to reduce oxidizing agents directly. The latter first oxidize KI in acidic solution and the iodine liberated is then titrated with thiosulphate. Hence, in titrations with thiosulphate, in addition to the solution of the oxidizing agent and the indicator (starch), a 5-10 per cent solution of KI and 2*N* solution of HCl or H_2SO_4 are also required.

Determination of the normality of the $Na_2S_2O_3$ solution against $K_2Cr_2O_7$ is based on the reaction

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + 3I_2 + 4K_2SO_4 + 7H_2O$$

$$\begin{array}{l|l} 1 & Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \\ 6 & I^- - e = I^0 \end{array}$$

From this reaction it can be seen that the gram-equivalent of $K_2Cr_2O_7$ is equal to $\frac{\text{mole}}{6}$.

Procedure. Dissolve in a graduated flask the amount of $K_2Cr_2O_7$ (accurately weighed on an analytical balance) needed to obtain an approximately 0.1*N* solution. Add

to a conical flask successively[1] 15-20 ml of 5-10 per cent KI solution , 30-40 ml of $2N$ H_2SO_4 solution, and a fixed volume of the $K_2Cr_2O_7$ solution taken by means of a pipette. Allow the mixture to stand for 3-5 minutes and then dilute with 100-150 ml of water. Titrate the iodine liberated with the $Na_2S_2O_3$ solution being standardized. At first titrate without any indicator until the solution is pale yellow in colour. Then add 2-3 ml of starch solution and continue to titrate with the sodium thiosulphate solution until the blue colour of the solution disappears. The solution will not be completely decolourized because the Cr^{3+} ion imparts a greenish colour to the solution.

In the presence of an excess of KI and H_2SO_4 the amount of iodine liberated is equivalent to the amount of $K_2Cr_2O_7$, and the amount of $Na_2S_2O_3$ solution used in the titration is equivalent to the quantity of iodine liberated. Hence, the volume of sodium thiosulphate solution used in the titration contains $Na_2S_2O_3$ in a quantity equivalent to that of the $K_2Cr_2O_7$ taken for analysis. Therefore,

$$\frac{V_{Na_2S_2O_3}}{V_{K_2Cr_2O_7}} = \frac{N_{K_2Cr_2O_7}}{N_{Na_2S_2O_3}}$$

The normality of the $Na_2S_2O_3$ solution is calculated from this formula. The titre of the $Na_2S_2O_3$ solution is usually expressed in terms of iodine:

$$T_{Na_2S_2O_3/I_2} = \frac{E_{I_2} \cdot N_{Na_2S_2O_3}}{1000} \text{ g/ml}$$

175. Standardization of Sodium Thiosulphate Solution Against Standard Permanganate Solution

Procedure. Place in a conical flask successively: 20.00 or 25.00 ml of standard $KMnO_4$ solution, 30-40 ml of $2N$ H_2SO_4 solution, and 15-20 ml of 10 per cent KI solution.

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[1] The following solutions must be added to the flask in the specified order to first make sure that on adding H_2SO_4 to the KI solution no iodine is liberated (the solution does not turn blue in the presence of starch indicator).

The equation for the reaction that takes place is

$$2KMnO_4 + 10KI + 8H_2SO_4 = 5I_2 + 2MnSO_4 +$$

$$+ 6K_2SO_4 + 8H_2O$$

After that allow the mixture to stand for 2-3 minutes, add 100-150 ml of water, and titrate with sodium thiosulphate, first without an indicator until the solution is pale yellow and then, after adding 2-3 ml of starch indicator, until the solution is completely decolourized.

The normality of the $Na_2S_2O_3$ solution is found from the formula:

$$V_{KMnO_4} \cdot N_{KMnO_4} = V_{Na_2S_2O_3} \cdot N_{Na_2S_2O_3}$$

176. Purification of Iodine

Commercial iodine is often contaminated with chlorine, bromine, water, and sometimes with cryanogen. Therefore, it is necessary to sublimate the iodine prior to using it for analysis. For this purpose, grind 5-6 g of commercial iodine in a mortar with 2 g of KI. The chlorine and bromine displace the iodine in the KI, forming nonvolatile potassium chloride and bromide. Transfer the resulting mixture to a dry wide-necked conical flask and close the latter loosely with a stopper carrying a large-bore test tube, the inside of which is continuously cooled with a jet of water. Place the flask on a sand bath or on an asebstos gauze and heat it over a slow flame. The iodine is rapidly sublimated and deposits on the cold walls of the test tube.

As soon as violet vapours of iodine are no longer liberated, discontinue sublimation. Allow the flask to cool. Carefully remove the test tube together with the iodine crystals adhering to it. Transfer the iodine crystals to a weighing bottle with the aid of a glass or porcelain spatula. Repeat this process to make sure that the iodine is pure. To remove any traces of water, grind the crystals in a mortar and dry during 24 hours on a watch glass placed in a desiccator charged with calcined $CaCl_2$. No lubricant should be applied to the lid.

177. Preparation of Iodine Solution

Iodine is only slightly soluble in water, but it readily dissolves in concentrated KI solutions to form the complex $[I_3]^-$ ion:

$$I_2 + KI \rightleftarrows K[I]_3$$

$$I_2 + I^- = [I_3]^-$$

Procedure. Weigh out on an analytical balance 2-3 g of crystalline KI in a weighing bottle. Dissolve the weighed portion in as little water as possible (2-3 ml). As soon as the weighing bottle attains ambient temperature (heat is absorbed when KI dissolves in water), close it and weigh on an analytical balance. Place the required amount of iodine in the weighing bottle (weighed together with KI), quickly close the latter and weigh it accurately. The difference between the two weighings is the mass of the iodine. Carefully agitate the mixture until the iodine has completely dissolved, i.e., until the minute particles on the walls of the weighing bottle disappear.[1] Transfer the solution through a funnel to a graduated flask, carefully wash the weighing bottle and funnel. Make up to the mark with water. Close the flask with a ground-glass stopper, and mix its contents thoroughly.

178. Standardization of Iodine Solution Against Standard Thiosulphate Solution

Procedure. Transfer a fixed volume of the prepared iodine solution to a conical flask and dilute with an approximately equal volume of water. Titrate with standard thiosulphate solution until the colour of the solution is pale yellow, then add 1-2 ml of starch indicator and continue to titrate until the solution is completely decolourized. The normality of the iodine solution is calculated from the equation:

$$N_{I_2} = \frac{V_{Na_2S_2O_3} \cdot N_{Na_2S_2O_3}}{V_{I_2}}$$

[1] If the iodine does not dissolve completely, add a little more KI after weighing.

179. Determination of Potassium or Sodium Sulphide in the Commercial Product

The iodometric determination of sulphides in acidic solution is based on the following reaction:

$$S^{2-} + I_2 = S + 2I^-$$
$$S^{2-} - 2e = S$$

Hence, the gram-equivalent of sulphide is equal to half its gram-molecule.

Procedure. Grind the sample of sulphide under test in a mortar. Prepare a solution of approximately the same normality as the standard thiosulphate solution. Pipette 20.00-25.00 ml of the prepared solution into a conical flask and add to it, with the aid of a pipette or burette, a fixed volume of standard iodine solution containing an excess of iodine as compared with the theoretically calculated (stoichiometric) quantity and about 10 ml of 2*N* HCl solution. The H_2S liberated is oxidized by the iodine to free sulphur. Add 1 g of sodium bicarbonate, $NaHCO_3$. Back titrate the excess of iodine with standard $Na_2S_2O_3$ solution (paying no attention to the sulphur precipitated). In a separate flask titrate with the same thiosulphate solution a volume of iodine solution equal to that added to the sulphide under test. The difference between the two titration results gives the volume that contains $Na_2S_2O_3$ in an amount equivalent to the sulphide being titrated.

Example. Suppose that 200 g of solution were prepared from 1.1296 g of Na_2S under test and to 25 ml of the resulting solution were added 40.00 ml of iodine solution. The amount of 0.1*N* $Na_2S_2O_3$ solution used to titrate the excess of iodine was 28.60 ml, whereas 38.70 ml were used to titrate 40.00 ml of iodine in the absence of sodium sulphide.

Hence, 25 ml of Na_2S solution is equivalent to 38.70—28.60 = 10.10 ml of $Na_2S_2O_3$ solution.

The titre of 0.1*N* $Na_2S_2O_3$ in terms of Na_2S is

$$T_{Na_2S_2O_3/Na_2S} = \frac{E_{Na_2S} \cdot N_{Na_2S_2O_3}}{1000} = \frac{E_{Na_2S} \cdot 0.1}{1000}$$

The gram-equivalent of Na_2S is equal to 0.5 mole:

$$E_{Na_2S} = \frac{78.06}{2} = 39.03 \text{ g}$$

Therefore,

$$T_{Na_2S_2O_3/Na_2S} = \frac{39.03 \times 0.1}{1000} = 0.003903 \text{ g/ml}$$

The amount of Na_2S contained in 25 ml of solution is 0.003903×10.10 g.

The weighed portion of sodium sulphide under test contains

$$\frac{0.003903 \times 10.10 \times 200}{25} = 0.3154 \text{ g } Na_2S$$

or

$$\frac{0.3154 \times 100}{1.1296} = 27.92\% \text{ } Na_2S$$

180. Determination of Percentage of Nitrites

A nitrite is readily oxidized by potassium permanganate in acidic solution:

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O$$

$$\begin{array}{r|l} 2 & MnO_4^- + 8H^+ + 5e = 2Mn^{2+} + 4H_2O \\ 5 & NO_2^- + H_2O - 2e = NO_3^- + 2H^+ \end{array}$$

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O$$

To a fixed volume of acidified $KMnO_4$ solution (taken in excess) add a fixed volume of the sodium nitrite solution prepared in a graduated flask. On adding KI solution to the mixture, the $KMnO_4$ unconsumed in the reaction oxidizes it and liberates free iodine which is titrated with standard $Na_2S_2O_3$ solution.

Procedure. Prepare in a graduated flask a nitrite solution of approximately the same normality as that of the $Na_2S_2O_3$ solution. The gram-equivalent of the nitrite is equal to 0.5 gram-molecule.

Pour 40 ml of standard $KMnO_4$ solution from a burette into a conical flask, add 10-15 ml of $2N$ H_2SO_4 solution and pipette a fixed volume (about 20 ml) of the prepared nitrite solution into it. Stopper the flask and shake carefully. Part of the $KMnO_4$ will react with the nitrite and part of it will remain unconsumed. To determine the excess of $KMnO_4$, add to the resulting solution 2 g of KI. Agitate the mixture and then allow it to stand for 2-3 minutes. Dilute

the solution with 100 ml of water and titrate the liberated iodine with standard $Na_2S_2O_3$ solution. Suppose that V_1 ml of $Na_2S_2O_3$ were used in the titration.

Into another flask pour from a burette the same volume of $KMnO_4$ solution (40 ml). Add 15-20 ml of $2N$ H_2SO_4 solution and 2 g of solid KI. Mix well and then allow to stand for 2-3 minutes. Add 100 ml of water and titrate with standard $Na_2S_2O_3$ solution. Suppose that V_2 ml of $Na_2S_2O_3$ were used in this titration.

The volume of $Na_2S_2O_3$ solution, equivalent to the volume of the nitrite solution, is equal to $V_2 - V_1$.

The titre of $Na_2S_2O_3$ in terms of $NaNO_2$ is

$$T_{Na_2S_2O_3/NaNO_2} = \frac{E_{NaNO_2} \cdot N_{Na_2S_2O_3}}{1000} \text{ g/ml}$$

The content of the nitrite in the volume of the sample taken for titration is

$$T_{Na_2S_2O_3/NaNO_2} \cdot (V_2 - V_1)$$

Calculate the content of nitrite in the sample and its percentage.

Questions and Problems

1. What standard solutions and indicator are used in iodometry?
2. Write the equation for the reaction between $Na_2S_2O_3$ and I_2. What oxidation-reduction process takes place?
3. What is the gram-equivalent of $Na_2S_2O_3$ in its reaction with iodine?
4. How are thiosulphate and iodine solutions standardized?
5. How is the content of an oxidizing agent determined by iodometric analysis?
6. How is the content of a reducing agent determined by iodometric analysis?
7. Why is an excess of KI used in iodometric analysis?
8. Why must acidic solutions be diluted with a large amount of water prior to titrating them with thiosulphate solution?
9. H_2SO_4 and an excess of KI were added to 30.00 ml of $0.107N$ $KMnO_4$ solution; suppose 33.27 ml of $Na_2S_2O_3$ solution were used to titrate the iodine liberated. Determine the normality of the $Na_2S_2O_3$ solution and its titre in terms of iodine.

Ans. $0.0965N$; 0.0122 g/ml

10. How many grams of $K_2Cr_2O_7$ are contained in a solution if, after adding excess KI and H_2SO_4 to it, 30.00 ml of $0.1N$ $Na_2S_2O_3$ solution were used to titrate the iodine liberated?

Ans. 0.147 g

CHAPTER XXXVIII

Precipitation Titrations — I Argentimetry (Mohr's Method)

181. General Principles of the Precipitation Method

Precipitation titrations are based on reactions that result in the formation of a difficultly soluble precipitate. Although such reactions are not uncommon, their use in titrations is limited. Not all precipitation reactions can be used in titrimetric analysis, because in some reactions the character of the precipitate formed and completeness of precipitation do not meet specified requirements and, moreover, it is difficult to find suitable indicators for determining the equivalence point of the reaction. In this book titrations with silver nitrate (Mohr's method) and with thiocyanate (Volhard's method) will be considered.

182. Principles of the Mohr Method

This method is based on the reaction of silver ions with halogen ions to form an insoluble silver salt, for example,

$$Ag^+ + Cl^- = AgCl\downarrow$$

Titrations are carried out with a standard $AgNO_3$ or NaCl solution. Mohr's method can be used to determine the content of chlorides and bromides (using a standard $AgNO_3$ solution) and silver salts (using a standard NaCl solution). When titrating a chloride or bromide solution, 1 or 2 drops of K_2CrO_4 are added to the solution and $AgNO_3$ solution is added from a burette, mixing constantly, until a persistent red-orange precipitate of Ag_2CrO_4 is formed.

In Mohr's method, titration is conducted only in neutral solution. Acidic solutions are previously neutralized with alkali in the presence of phenolphthalein indicator and then dilute acetic acid is added until the solution is decolourized. This method cannot be applied to acidic and alkaline solutions. Ag_2CrO_4 is soluble in acids; this makes it impossible to determine the equivalence point precisely.

In strongly alkaline solutions the Ag^+ ion reacts with OH^- ion to form AgOH which is then converted to Ag_2O:

$$Ag^+ + OH^- = AgOH; \quad 2AgOH = Ag_2O + H_2O$$

183. Preparation of Silver Nitrate Solution and Potassium Chromate Indicator

Calculate the weighed portion of $AgNO_3$ needed to prepare 1 litre of 0.05*N* solution:

$$E_{AgNO_3} = M_{AgNO_3} = 169.88 \text{ g}$$

Hence, to prepare 1 litre of 0.05*N* $AgNO_3$ solution, $169.88 \times 0.05 = 8.494$ g of the salt are required. As chemically pure $AgNO_3$ is not available, standard solutions of approximate concentration are prepared: weigh out 8-9 g of $AgNO_3$ on a rough balance and dissolve in 1 litre of water (measured in a graduated cylinder). Mix well and keep the solution in a dark glass bottle.

To prepare the K_2CrO_4 indicator, dissolve 10 g of chemically pure salt in 100 ml of water. For each titration, 1 or 2 drops of the indicator is added to the solution being titrated.

184. Standardization of Silver Nitrate Solution Against Sodium Chloride

First calculate the weighed portion of NaCl needed to prepare a solution of approximately the same normality as the standard $AgNO_3$ solution:

$$E_{NaCl} = M_{NaCl} = 58.44 \text{ g}$$

Consequently, to prepare 1 litre of 0.05*N* NaCl solution it is necessary to take 2.9220 g of salt. When the solution is prepared in a 250-ml graduated flask, 0.7305 g of NaCl is required.

Weigh out from 0.6 to 0.8 g of NaCl on an analytical balance to the nearest 0.0002 g, transfer the weighed portion through a funnel to a graduated flask and dissolve in distilled water. Make up to the mark with water, tightly stopper the flask, and mix its contents thoroughly. Calculate the

normality of the resulting NaCl solution from the mass of the weighed portion.

Procedure. Pipette a fixed volume of the NaCl solution (20.00 or 25.00 ml) into a conical flask, add 1 or 2 drops of K_2CrO_4 indicator, and dilute the solution with a quantity of water approximately equal to that of the solution under test. To the flask gradually add $AgNO_3$ solution from a burette until a persistent red-orange precipitate of Ag_2CrO_4 is obtained.

During titration, place the flask on a sheet of white paper and agitate constantly. Repeat titration three times; the test results should differ by not more than 0.1 ml.

The normality of the standard solution of $AgNO_3$ is

$$N_{AgNO_3} = \frac{N_{NaCl} \cdot V_{NaCl}}{V_{AgNO_3}}$$

The titre of the $AgNO_3$ solution in terms of NaCl is

$$T_{AgNO_3/NaCl} = \frac{E_{NaCl} \cdot N_{AgNO_3}}{1000}$$

Example. Suppose that 0.7178 g of chemically pure NaCl was weighed on an analytical balance and 250 ml of solution were prepared from it. The normality of the resulting solution is

$$\begin{array}{r} 0.7305 \text{ g NaCl} — 0.05N \\ 0.7178 \text{ g NaCl} — \quad xN \\ \hline x = \dfrac{0.05 \times 0.7178}{0.7306} = 0.04912N \end{array}$$

The ratio of the volumes at which the solutions are equivalent can be found by titrating the prepared NaCl solution with the $AgNO_3$ solution.

185. Determination of Percentage of Chlorides

Quantitative determination of chlorides by Mohr's method is conducted only in neutral solution. First calculate the weighed portion of the sample under test required to prepare a solution of approximately the same normality as that of the standard $AgNO_3$ solution. Then accurately weigh out on an analytical balance a weighed portion close to the

calculated one, transfer it quantitatively to a graduated flask and dissolve in distilled water. Stopper the flask tightly and mix well. Titrate a fixed volume of the resulting solution with the $AgNO_3$ solution in the presence of 1 or 2 drops of 10 per cent K_2CrO_4 solution.

Calculate the normality of the solution, the content of chloride in the weighed portion, and the percentage of chloride in the sample under test.

Example. Determine the percentage of KCl in the commercial product.

$$E_{KCl} = M_{KCl} = 74.56 \text{ g}$$

Hence, $74.56 \times 0.05 = 3.7280$ g of KCl must be taken to prepare 1 litre of $0.05N$ KCl solution and, therefore, to prepare 250 ml of $0.05N$ KCl solution, 0.9320 g of the salt is required.

Suppose that 0.9320 g of KCl weighed out on an analyticl balance was dissolved in water in a 250-ml flask and 21.30 ml (mean value) of standard $0.05141N$ $AgNO_3$ solution was used to titrate 25.02 ml of the KCl solution. The titre of the standard $AgNO_3$ solution in terms of KCl is

$$T_{AgNO_3/KCl} = \frac{E_{KCl} \cdot N_{AgNO_3}}{1000} = \frac{74.55 \times 0.05141}{1000} = 0.003833 \text{ g/ml}$$

Therefore, the weighed portion contains

$$\frac{0.003833 \times 21.3 \times 250}{25.02} = 0.8163 \text{ g KCl}$$

and the percentage of KCl in the sample is

$$\frac{0.8163 \times 100}{0.9319} = 87.60\%$$

Questions and Problems

1. What standard solutions and indicators are used in argentimetric titrations?
2. What substances are determined by argentimetric analysis?
3. In what cases is the argentimetric method unsuitable for determining the content of chlorides?
4. How is the $AgNO_3$ solution standardized?
5. What is meant by the titre of $AgNO_3$ in terms of NaCl?

6. How many grams of $AgNO_3$ are needed to prepare 5 litres of 0.5*N* solution?
Ans. 424.70 g
7. Determine the normality of a sodium chloride solution that contains 1.4615 g of NaCl in 200 ml of solution.
Ans. 0.125*N*
8. Calculate the normality of a $AgNO_3$ solution whose titre is equal to 0.00850 g/ml.
Ans. 0.0500*N*
9. Calculate the normality of a $AgNO_3$ solution whose titre in terms of NaCl is equal to 0.002923 g/ml.
Ans. 0.0500*N*
10. Determine the normality of a solution of $AgNO_3$ if it is known that 18.30 ml of the solution were used to titrate 20.00 ml of a KCl solution containing 2.3804 g of KCl in 250 ml of solution.
Ans. 0.1400*N*

CHAPTER XXXIX

Precipitation Titrations — II
Titrations with Thiocyanate (Volhard's Method)

186. Principles of the Volhard Method

This method is based on the reaction between silver ion and thiocyanate ion to form insoluble silver thiocyanate:

$$Ag^+ + SCN^- = AgSCN\downarrow$$

Titrations are carried out with a standard $AgNO_3$ solution and a standard solution of KSCN or NH_4SCN. Ferric-ammonium sulphate, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, is used as indicator. The end-point of titration is indicated by the appearance of a persistent reddish colour due to the formations of the complex ferric thiocyanate ion, $[Fe(SCN)_6]^{3-}$. The equations for the reaction are

$$3NH_4SCN + NH_4Fe(SO_4)_2 = Fe(SCN)_3 + 2(NH_4)_2SO_4$$
$$Fe(SCN)_3 + 3NH_4SCN = (NH_4)_3[Fe(SCN)_6]$$

Titrations with thiocyanate are used for the determination of halides, cyanide, cyanate, and silver. This method is used more often than the argentimetric method because the latter method can be used only in neutral solution, while the former can be used in acidic solution too. It can be applied to alkaline solutions only after neutralizing excess

OH^- ions. The method cannot be employed in the presence of oxidizing agents and mercury salts because oxidizing agents decompose the SCN^- ion and mercury precipitates it.

187. Determination of Silver Salts and Chlorides

Analysis of silver salts by means of titrations with thiocyanate should always be carried out in the following order: to the solution of the silver salt contained in a conical flask add 2-3 ml of the indicator (ferric-ammonium sulphate) and then standard thiocyanate solution from a burette until a persistent reddish colour appears.

Halide ions do not react with SCN^- ions; therefore, the Volhard method is conducted indirectly, by back titration. Add to a fixed volume of the halide solution an excess of $AgNO_3$ solution from a burette or by means of a pipette. Part of the $AgNO_3$ reacts with the halide ions to form an insoluble compound. Then titrate the unconsumed excess of Ag^+ with the thiocyanate solution. The content of halides is calculated from the equation

$$Ag^+ + X^- = AgX\downarrow$$

where X^- is the halide ion, and

$$Ag^+ + SCN^- = AgSCN\downarrow.$$

The amount of $AgNO_3$ that reacts with the halide is found as the difference between the known amount of $AgNO_3$ added and the excess of $AgNO_3$, determined by titration.

188. Preparation of Thiocyanate Solution and Ferric-Ammonium Sulphate Indicator

The concentration of the thiocyanate solution should be not less than $0.05N$, because it is difficult to determine the equivalence point at lower concentrations. Calculate the weighed portion of thiocyanate required to prepare 1 litre of, say, $0.05N$ solution. The thiocyanate is rarely chemically pure due to its hygroscopic nature. Therefore, the solution must be standardized against $AgNO_3$ solution. The portion of thiocyanate is weighed on a rough balance.

Example. It is required to prepare 1 litre of approximately 0.05*N* NH_4SCN solution.

$$E_{NH_4SCN} = M_{NH_4SCN} = 76.12g$$

Hence, 3.806 g of ammonium thiocyanate are needed to prepare 1 litre of 0.05*N* solution. Practically, a weighed portion of 4 g is taken.

To prepare the ferric-ammonium sulphate solution[1], dissolve 50 g of finely ground alum in 100 ml of water heated to boiling. Cool the solution; part of the alum is crystallized and is separated by filtration or decantation.

Standard ferric-ammonium sulphate solution is brown in colour due to hydrolysis of the basic ferric salt:

$$Fe_2(SO_4)_3 + 2H_2O \rightleftharpoons 2Fe(OH)SO_4 + H_2SO_4$$

As the reaction is reversible, hydrolysis can be depressed by acidifying the solution. Usually 5-6 ml of concentrated HNO_3 solution are added because this acid, unlike other mineral acids, does not form with silver ions an insoluble compound. Excess HNO_3 does not interfere with the reaction but, on the contrary, yields more precise results, because it decomposes the complex salts ($KSCN \cdot AgSCN$, $NH_4SCN \cdot AgSCN$) which may form in the solution. For each titration, 2-3 ml of the indicator and 5-6 ml of 6*N* HNO_3 solution are added.

189. Standardization of Thiocyanate Solution Against Standard Silver Nitrate Solution

The following reaction is utilized for standardizing the thiocyanate solution:

$$Ag^+ + SCN^- = AgSCN$$

Procedure. Dilute 20.00-25.00 ml of standard $AgNO_3$ solution with approximately the same volume of water. Add 2-3 ml of ferric-ammonium alum and 5-6 ml of 6*N* HNO_3 solution. Add from a burette, in small portions, potassium or ammonium thiocyanate, mixing constantly. Add thiocyanate solution until a reddish colour appears that

[1] Ferric-ammonium sulphate is less hydrolyzed in aqueous solution than other ferric salts.

persists after mixing vigorously. The colour of the solution is more discernible if the flask with the test solution is placed on a white background (a sheet of white paper) and the precipitate is allowed to settle.

The normality and titre of the solution are calculated from the following equation:

$$V_{NH_4SCN} \cdot N_{NH_4SCN} = V_{AgNO_3} \cdot N_{AgNO_3}$$

190. Determination of Silver in Alloys

Procedure. Weigh out on an analytical balance 0.5-1.0 g of ground alloy in the form of fine filings or turnings. Place the weighed portion in a 50-100 ml evaporating dish and add to it 20-30 ml of HNO_3 (sp gr 1.2). Cover the dish with a watch glass and heat gently until the alloy is completely dissolved. Uncover the dish and wash down the drops of liquid adhering to the watch glass into the dish. Evaporate the solution almost to dryness to remove excess HNO_3 and oxides of nitrogen. Dilute the solution with water and carefully transfer it to a graduated flask, washing the inside of the dish with distilled water. Make the solution up to the mark. Pipette a fixed volume of the prepared solution into a conical flask, dilute with any volume of water and titrate with standard thiocyanate solution.

Example. A sample of silver alloy weighing 0.7915 g was dissolved in water and diluted to a volume of 200 ml. On titrating the resulting solution with 0.05290*N* NH_4SCN solution, 27.20 ml were used to titrate 50.00 ml of the solution.

The titre of the NH_4SCN solution in terms of silver is

$$T_{NH_4SCN/Ag} = \frac{E_{Ag} \cdot N_{NH_4SCN}}{1000} = \frac{107.87 \times 0.0529}{1000} =$$

$$= 0.00571 \text{ g/ml}$$

The mass of silver equivalent to 27.20 ml of NH_4SCN solution is

$$0.00571 \times 27.20 = 0.1553 \text{ g}$$

This is the quantity of silver contained in 50 ml of solution prepared from the alloy.

The mass of silver in all of the solution prepared (i.e., in the weighed portion of the alloy under test) is

$$\frac{0.1553 \times 200}{50} = 0.6212 \text{ g} \quad \text{or} \quad \frac{0.6212 \times 100}{0.7915} = 78.48\%$$

CHAPTER XL

Complexometric Titrations

191. General Principles

Complexometric titrations (also called chelatometric titrations) are based on the formation of a stable water-soluble complex when the substance in the standard solution reacts with the cations under test. Although no precipitate is formed in the course of titration, the concentration of the ion being determined decreases as it is complexed. In this respect the process of complex formation resembles precipitation reactions. Precipitation is the more complete, the lower the solubility of the precipitate. The ion under test is complexed more completely the stronger (more stable) the complex, i.e., the lower the value of its instability constant.

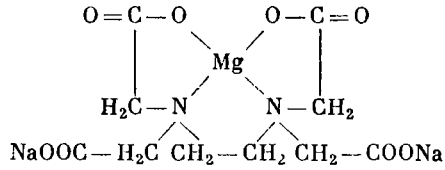
Recently, a new class of organic reagents have found wide applications for chemical analysis, the so-called 'complexones':

Most of the complexones are derivatives of iminodiacetic acid, $HN(CH_2COOH)_2$. The most widely used complexone is Versene (EDTA), the disodium salt of ethylenediaminetetraacetic acid:

$$\begin{array}{l} HOOC-CH_2-N-CH_2-CH_2-N-CH_2COOH \\ \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2-COONa \quad CH_2-COONa \end{array}$$

Versene forms stable water-soluble complexes with certain metal ions such as magnesium, alkaline earth metals, manganese, the rare metals. In complex formation the metal ion displaces the hydrogen in the carboxyl groups of the complexone and is attached by coordinate bonds with the nitrogen ions of Versene. For example, the magnesium

complex with Versene has the following structure:



The process of complex formation can be represented by the reaction

$$Mg^{2+} + Na_2H_2V \rightleftarrows Na_2[MgV] + 2H^+$$

Where Na_2H_2V represents the disodium salt of ethylenediaminetetraacetic acid.

To shift the equilibrium in the direction of complex formation it is necessary to bind the hydrogen ions. This is achieved by adding ammonia-ammonium chloride buffer solution, $NH_4OH + NH_4Cl$, which provides a sufficiently high pH.

The value of the instability constant of such complexes is very low: from 10^{-9} to 10^{-18}. In particular, the instability constant of the calcium complex is 2.6×10^{-11}; of the magnesium complex, 2×10^{-9}.

The indicators used in complexometric titrations are organic reagents that give with the metal ion under test compounds of a characteristic colour. This colour differs sharply from the colour of the indicator itself. The colour of the test solution changes (the indicator reverts to its original colour) close to the equivalence point when almost all the cations being determined are bound in the complex with Versene, i.e., when the concentration of the metal ions is sharply decreased.

In other titration methods the indicator usually forms a coloured compound with the ions contained in the standard solution (for example the K_2CrO_4 indicator in precipitation titration). In complexometric titrations use is made of an indicator that forms a coloured compound with the ion being determined. Such an indicator is Eriochrome Black T (alizarin chrome black) which forms with magnesium, calcium and certain other metal ions complexes that are intense

wine-red in colour. The indicator not bound in the complex is blue in colour. Eriochrome Black T is a sensitive indicator because the change in colour from wine-red to blue is very sharp.

192. Preparation of Standard Versene (EDTA) Solution

The standard Versene solution is prepared from an accurately weighed portion of disodium EDTA (dihydrate), $Na_2H_2V \cdot 2H_2O$. The gram-equivalent of Versene is equal to 0.5 mole of $Na_2H_2V \cdot 2H_2O$:

$$M_{Na_2H_2V} = 372.3; \quad E_{Na_2H_2V} = 186.15$$

Usually a 0.05*N* solution is used, prepared by dissolving 9.3075 g in a 1-litre graduated flask.

The solution is standardized against a solution of a magnesium or calcium salt of exactly known concentration, for instance, a magnesium sulphate solution prepared from a primary standard contained in an ampoule ('fixinal').

193. Preparation of Eriochrome Black T Indicator and Ammonia-Ammonium Chloride Buffer

Eriochrome Black T in the solid state is stable, but its solutions are stable only for a few days.

Usually a mixture of solid Eriochrome Black T and sodium or potassium chloride (in a ratio 1 : 200) is used. The mixture is finely ground in a mortar and kept in a dark glass bottle with a ground-in stopper. This mixture is stable indefinitely. For each titration, 20-30 mg of the prepared mixture is used per 100 ml of solution being titrated.

Alcoholic solutions of this indicator are also used. They are prepared as follows: dissolve 0.5 g of Eriochrome Black T in 10 ml of ammonia-ammonium chloride buffer (prepared as described below) and dilute to 100 ml with ethyl alcohol. This solution is stable during 10 days.

To prepare the buffer solution, dissolve 54 g of ammonium chloride in 350 ml of concentrated ammonia solution and dilute to 1 litre with distilled water.

194. Determination of Water Hardness (Total)

When total water hardness is determined by neutralization in a previously neutralized sample under test, improper neutralization of the sample may considerably affect the test results.

This source of error can be avoided if titration with Versene is used to determine the water hardness. Besides, this method takes very little time.

Procedure. Measure out 100 ml of the water under test into a graduated flask. Add 5 ml of the buffer solution to it and then 7 or 8 drops of the alcoholic indicator solution or a pinch of the mixture of solid indicator and NaCl or KCl. After mixing thoroughly, the solution will be wine-red in colour. Titrate the mixture with 0.0500*N* Versene solution. Towards the end of titration add the titrant dropwise, shaking the flask after adding each drop. Titrate until, on adding one drop of the Versene solution, the wine-red colour changes to blue with a greenish tint and the addition of an excess drop of titrant does not change the colour.

The total water hardness is calculated from the formula

$$H_T = \frac{N_{Versene} \cdot V_{Versene} \cdot 1000}{V_{water}} \text{ mg-equiv/lit}$$

where $N_{Versene}$ = normality of Versene;
$V_{Versene}$ = number of millilitres of Versene used in the titration;
V_{water} = number of millilitres of water taken for the analysis.

GAS ANALYSIS

CHAPTER XLI

General Principles

195. Methods of Gas Analysis

Gas analysis is one of the methods of quantitative analysis. It consists in the measurement of the volume or mass of the components of a gas mixture or the gas evolved in a chemical reaction. There are three methods of gas analysis: absorptiometric, combustion, and analytical methods.

In the *absorptiometric method* a measured volume of gas is brought into intimate contact with various reagents in special apparatuses and the reduction in volume is measured after each absorption process. The analysis is carried out as follows. A gas burette is filled with the gas under test which is then transferred to an absorption bottle containing a suitable absorbent where the component being determined is dissolved or converted to a nonvolatile compound. The remaining gas (that has not been absorbed) is returned to the gas burette and the volume of the gas absorbed is determined by the difference between the gas volumes before and after treatment with the respective absorbent. This method is used to determine the content of oxygen, carbon monoxide and dioxide, hydrogen sulphide, unsaturated aliphatic hydrocarbons (acetylene, ethylene), and other gases.

Hydrogen, methane, and a number of other gases for which there are no suitable absorbents are analyzed by the *combustion method.* In this method a measured volume of the gas mixture under analysis is mixed with a definite volume of oxygen or air. The resulting mixture is burned in the presence of a catalyzer and the content of the burnt component is calculated by the reduction in volume.

For example, on burning hydrogen, the reaction is

$$2H_2 + O_2 = 2H_2O$$

in which two volumes of hydrogen react with one volume of oxygen to produce water vapour. The latter condenses forming liquid water, the volume of which is negligible and can be disregarded. Consequently, after cooling the remaining gas to the initial temperature, the volume of the gas will be reduced by three volumes, two thirds of which is the volume of hydrogen contained in the original mixture.

On burning methane, the reaction is

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Thus, three volumes of the gas being burned yield one volume of carbon dioxide equal to the volume of methane, and the decrease in volume is equal to twice the volume of carbon dioxide.

In the *analytical method* the volume of gas liberated by a chemical reaction is measured and the mass of the substance

that liberates the gas is determined by the volume of the gas liberated. For example, limestone reacts with hydrochloric acid to form carbon dioxide:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

The volume of gas liberated is reduced to standard conditions, i.e., corrected for a temperature of 0°C and a pressure of 760 mm Hg and then the calcium carbonate content is determined from the following formula:

$$V_0 = \frac{V \cdot 273 (B - P)}{(273 + t) \cdot 760}$$

where V_0 = volume of gas under standard conditions;
V = measured volume of gas, ml;
t = temperature of gas, °C;
B = barometric pressure, mm Hg;
P = water vapour tension at testing temperature, mm Hg.

196. Sampling and Storage of Samples

A sample of the gas under analysis is taken with a gas pipette or gasometer.

A gas pipette is a vessel provided at both ends with glass stopcocks or rubber tubes stoppered with glass rods or pinch clips. The gas can be drawn into the pipette with the aid of a sealing liquid (Fig. 32) as follows. Connect the lower end of the pipette to an equalizing bottle filled with water. Open both stopcocks and fill the pipette with water by lifting the equalizing bottle until water begins to flow out of the top stopcock, then close the stopcocks. Connect the top of the pipette by means of a capillary tube to the container with the gas under analysis and open the stopcocks; the water is drained from the pipette and the gas is sucked into the pipette.

Ten and more litres of gas are stored in a gasometer made of sheet metal or glass and provided with a water gauge on one side (Fig. 33). The gasometer is first filled with water in the following way. Pour water into funnel *4*, close branch tube *6* and open stopcocks *3* and *5*. The water will flow into the lower vessel through tubes *2*, one of which

reaches the bottom of the gasometer, while the other terminates at the outlet of the gasometer. The air expelled by the water passes through cock *5*. Add water until it begins to flow through cock *5* and then close the latter. Close cock *3* only when air escapes through the top funnel from the bottom of tube *2*. Some water should be left in the funnel. To fill the gasometer with gas, close the stopcocks and open

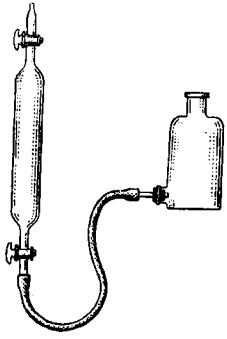


Fig. 32. Gas pipette and equalizing bottle

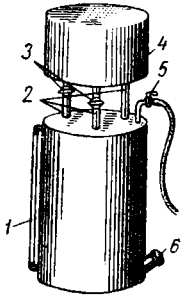


Fig. 33. Gasometer
1 — water gauge; *2* — tubes; *3*, *5* — stopcocks; *4* — funnel; *6* — branch pipe

branch tube *6*. If the gasometer is airtight no water will flow out. Insert the gas delivery pipe into tube *6*. The gas will collect in the upper part of the gasometer and displace the water which flows out of tube *6*. The volume of gas collected in the gasometer is determined by the water level in water gauge *1*. After filling the gasometer with gas, stopper tube *6*. In this way the gasometer can be filled with gas at a gauge pressure exceeding atmospheric pressure. If it is necessary to fill the gasometer with air or some other gas at a pressure equal to or less than atmospheric pressure, connect the gas delivery tube to opened stopcock *5* and open tube *6*, first making sure that stopcocks *3* are closed. Water flowing from tube *6* sucks the gas into the gasometer. When gas-filling is completed, close tube *6* and stopcock *5*. To transfer gas from the gasometer to some other vessel, fill funnel *4* to the top with water, open stopcocks *3* and thus produce a pressure in the gasometer,

thanks to which the gas is expelled through stopcock *5*. Steadily replace the water in funnel *4* as it flows out. After the gas is transferred to the apparatus, close all the stopcocks.

197. Gas Analyzer

The percentage of the individual components of a gas mixture containing carbon dioxide, oxygen, and carbon monoxide is determined with the aid of a gas analyzer of the simplest construction, used to analyze flue and producer gases. The apparatus is compact, rugged, and easily transported. It is contained in a portable wooden case.

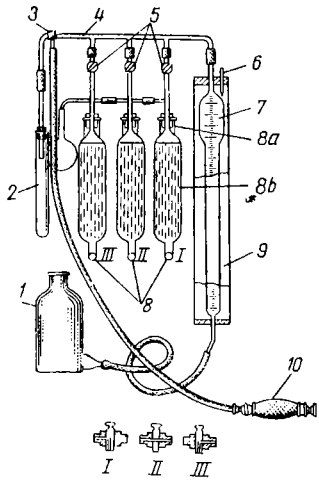


Fig. 34. Schematic drawing of a gas analyzer

1 — equalizing bottle; *2* — gas filter; *3*, *5* — stopcock; *4* — manifold pipe; *6* — thermometer; *7* — graduated burette; *8* (*III*, *II*, *I*) — absorption vessels (*8a* — back cylinder; *8b* — front cylinder); *9* — water jacket; *10* — rubber bulb; *I*, *II*, *III* — positions of stopcock

A schematic drawing of the gas analyzer is shown in Fig. 34. The analyzer consists of graduated burette *7*, manifold pipe *4*, three absorption vessels (including back cylinder *8a* and front cylinder *8b*), equalizing bottle *1*, gas filter *2*.

Graduated burette *7* is used to measure the original volume of the gas mixture under test and the volumes obtained after the gases are absorbed by suitable absorbents. It is enclosed in water jacket *9* (which is a large-bore cylinder filled with water) to maintain a constant temperature. Thermometer *6* is inserted in the top of the water jacket. The burette is of 100 cm^3 capacity. The bulb in the upper portion of the burette is approximately 50 cm^3 in capacity and the narrow portion is graduated in 0.2-cm^3 divisions. The bottom of the burette is connected by a rubber tube to equalizing bottle *1*, and the top to manifold pipe *4*.

Manifold pipe *4* used for distributing the gas to the various parts of the gas analyzer is a thick-walled capillary tube with three capillary outlets provided with stopcocks *3* and *5*. These outlets are connected to vessels *8* by means of small-bore, thick-walled rubber tubing. One end of the manifold is connected to the graduated burette; the other end is fitted with three-way cock *3* by means of which the gas analyzer can be connected to the gas supply or to the atmosphere.

Three-way cock *3*, on changing its position, connects the graduated burette to the gasometer or the atmosphere or disconnects it completely, thus isolating the inner part of the apparatus. In position *I* the cock is closed and the inner part of the apparatus is completely isolated. In position *II* the cock connects the graduated burette via tube *2* to the gasometer with the gas sample. In position *III* the graduated burette is connected through the pipe to the atmosphere.

Each absorption vessel *8* consists of two joined glass cylinders (back cylinder *8a* is behind front cylinder *8b* and is not visible in the drawing). Front cylinder *8b* receives the gas during the absorption process; back cylinder *8a* receives the absorbent when the front cylinder is being filled with the gas. The capacity of the absorption vessel is 200 cm^3. Each vessel is marked with the letter *M*. In order to increase the contact surface of the absorbent and the gas under test, cylinder *8a* is filled with small glass thin-walled (0.3-0.6 mm thick) tubes of an external diameter of 4-5 mm. Cylinder *8a* is provided with a capillary tube at the top which is attached to the manifold outlet by rubber tubing and stopcock *5*. The top of cylinder *8b* is closed with a rubber stopper carrying a tube covered with a small rubber bag for protecting the reagents from penetration of air.

The glass parts of the gas analyzer are butt-joined with flexible rubber tubes.

Equalizing bottle *1* of a capacity not less than 300 cm^3 is filled 3/4 of its volume with the sealing liquid which is usually a 10 per cent solution of sulphuric acid to which 1-2 ml of methyl orange indicator has been added. The equalizing bottle is used for sucking the gas into the gra-

duated gas burette and delivering it to one or another absorption vessel for analysis. It also equalizes the pressure within the burette.

198. Preparation of Solutions for Absorption of Carbon Dioxide, Oxygen, and Carbon Monoxide

Absorbents are prepared from reagents capable of combining chemically with a given gas. Careful attention must be paid to the order in which the gas sample is exposed to the reagents in order to be able to determine the content of each component by the decrease in volume of the gas mixture under analysis. If it is expected that the gas mixture simultaneously contains carbon dioxide, oxygen, and carbon monoxide, the following sequence must be observed: (1) carbon dioxide, (2) oxygen, (3) carbon monoxide, because the first absorbent (KOH solution) absorbs only CO_2, while the second absorbent (alkaline solution of pyrogallol) absorbs O_2 and CO_2, and the third absorbent (ammoniacal solution of cuprous chloride) absorbs CO and CO_2. The best absorbent for carbon dioxide is 30-35 per cent potassium hydroxide solution which reacts with CO_2 as follows:

$$2KOH + CO_2 = K_2CO_3 + H_2O$$

Sodium hydroxide should not be used because the sodium carbonate which is formed on absorbing CO_2 is sparingly soluble in concentrated NaOH solution and the capillary tubes and cocks of the apparatus become blocked up.

It should be taken into account that the alkali solution can absorb, in addition to CO_2, other gases, such as hydrogen chloride, chlorine, hydrogen sulphide, and sulphur dioxide.

Porcelain ware must be used to prepare the alkali solution. Glassware is not suitable for this purpose because the great heat of solution of alkalies may give rise to hot spots which ordinary glass does not withstand. Besides that, glass dissolves in concentrated alkali solution.

Oxygen is absorbed by an alkaline solution of pyrogallol (1,2,3 — trihydroxybenzene, $C_6H_3(OH)_3$) which is a power-

ful reducing agent. To prepare the solution, proceed as follows. First prepare separately a potassium hydroxide solution (120 g of KOH in 80 cm^3 of water) and then an aqueous solution of pyrogallol (50 g of pyrogallol in 1000 cm^3 of hot water). Mix the two solutions immediately prior to filling the absorption vessel of the apparatus because, on standing, the alkaline pyrogallol solution is readily oxidized by atmospheric oxygen and, hence, its absorptive power is markedly diminished.

The absorbent for carbon monoxide is an ammoniacal solution of cuprous chloride. It forms, on absorbing carbon monoxide, a complex compound:

$$Cu_2Cl_2 + 2CO = Cu_2Cl_2 \cdot 2CO$$

The ammoniacal solution of Cu_2Cl_2 is prepared by dissolving 32 g of Cu_2Cl_2 in 110 cm^3 of 25 per cent aqueous ammonium chloride solution and adding, stirring constantly, 80-100 cm^3 of concentrated ammonia solution until a clear bright blue solution is obtained. As cuprous ions are readily oxidized by atmospheric oxygen, metallic copper (in the form of chips or wire turnings) is added to the bottle containing the ammoniacal solution. Moreover, the solution is covered with a 2-3 cm layer of mineral oil to prevent it from coming into contact with the air.

199. Assembly of Gas Analyzer and Preparation for Analysis

When assembling the gas analyzer, pains must be taken to carefully clean the apparatus and lubricate the stopcocks.

Cleaning the gas analyzer. Prior to assembling the apparatus, all the glass parts must be thoroughly washed as follows: remove the grease from the stopcocks with acetone, wash the apparatus successively with warm alkali solution, tap water, warm dichromate-sulphuric acid solution, again with tap water, and finally with distilled water. The vessel is deemed to be clean only after the water drains completely, without leaving any drops on the walls.

It is recommended that the parts of the gas analyzer be dried in a stream of warm air rather than in a drying cabinet.

The glass parts of the gas analyzer are butt-joined by means of flexible rubber tubing.

Lubrication of stopcocks. The tap and socket must be previously washed with acetone and dried. The grooves of the stopcock are wiped free from grease with cotton wool wrapped on a copper wire. Grease should not be applied to the entire surface of the tap; a thin layer is applied to the upper and lower part of the barrel which is then placed in the socket and turned until it becomes transparent. Lanolin is used as the lubricant; it is previously dehydrated in a drying cabinet at a temperature of 100°C during 25-30 hours. Other lubricants can also be used, for instance, one prepared in the following way: heat in an evaporating dish *1* part by weight of wax and *4* parts by weight of white petrolatum, then mix the molten mass thoroughly, and cool. The use of petrolatum alone as lubricant is not recommended because it does not insure sufficient tightness due to its low viscosity.

Preparation of apparatus for work. Pour the sealing liquid into equalizing bottle *1* (see Fig. 34) so that it is 3/4 full, fill water into jacket *9*, and into each of the absorption vessels 200 cm^3 of the respective absorbent: alkali hydroxide in vessel *I*, alkaline solution of pyrogallol in vessel *II*, and ammoniacal solution of cuprous chloride in vessel *III*. Turn stopcock *3* to position *III* to allow air to enter the gas analyzer; then raise the equalizing bottle to fill the gas burette with the sealing liquid to the top division mark and set stopcock *3* in position *I* to cut off the gas analyzer from the atmosphere. Open stopcock *5* to connect absorption vessel *C* to the burrette and, slowly lowering the equalizing bottle, bring the level of the absorbent to the mark *M*, then close stopcock *5*. Fill absorption vessels *III* and *II* in the same way.

The assembled gas analyzer must be tested for tightness. For this purpose, after filling all three absorption vessels to the mark on the upper capillary tubes, fill the graduated gas burette with the sealing liquid to the top division, lower the equalizing bottle, and allow the apparatus to stand for 5-10 minutes; the level of the liquid in the burette and in the absorption vessels should not change. Otherwise all the joints of the absorption vessels with the manifold pipe must be checked for tightness.

200. Analysis of a Gas Mixture

Filling the burette with the gas under analysis. Turn stopcock *3* to position II to connect the burette to the gas supply via the gas filter. Lower the equalizing bottle slowly to fill the burette with the gas. This portion of gas will contain the air that filled the manifold pipe, rubber tubes, and gas filter. Therefore, turn stopcock *3* to position *III* and raise the equalizing bottle to expel the first portion of gas into the exhaust hood. This procedure is repeated 4 or 5 times. Filling is completed only after thoroughly 'rinsing' the system with the gas under test. Fill the burette with the gas to a height a little lower than the 100-cm^3 mark and set the equalizing bottle so that the level of the liquid in it coincides with the 100-cm^3 mark of the graduated burette. Then quickly turn stopcock *3* to position *III* to give air access to the burette for an instant, and as soon as the liquid reaches the 100-cm^3 mark in the burette, close the stopcock. In this way the 100 cm^3 of the gas taken for analysis in the burette are brought to atmospheric pressure.

Analysis of the gas under test. First determine the content of carbon dioxide as follows. Pass the gas into absorption vessel *I* filled with the alkali solution. To do this, raise the equalizing bottle, open the stopcock of the manifold leading to this vessel and expell all the gas from the burette into the vessel. After that, lower the equalizing bottle until the level of the absorbent reaches mark *M*; then close the stopcock, allow the liquid to drain down the burette walls, and measure the volume of the remaining gas. In all measurements care should be taken that the liquid in the burette and in the equalizing bottle are at the same level. The absorption procedure is repeated several times until the volume of the gas in the burette attains a constant value. After that, in the same manner, oxygen is absorbed by transferring the gas to vessel *II* containing the alkaline solution of pyrogallol. The gas should be slowly passed into the vessel and back into the burette a greater number of times than when determining CO_2; it is even recommended that the gas be allowed to stand for 3-4 minutes in the absorption vessel each time, because absorption of oxygen proceeds rather slowly.

After the oxygen is completely absorbed, transfer the remaining gas several times to vessel *III* containing the ammoniacal solution of cuprous chloride.

The content of the components in the gas mixture is calculated by the reduction in volume of the gas after each absorption process. The quantitative composition of the gas mixture is expressed as per cent by volume. Thus, if the volume of the gas mixture was 100 cm^3 and after it was passed through potassium hydroxide solution it was reduced to 70 cm^3, the percentage of carbon dioxide will be

$$\frac{(100-70)\times 100}{100}=30\%$$

The volume of a given quantity of gas is considerably affected by even slight changes in pressure and temperature. However, in the above gas analysis this is of no importance, because the volume of the components changes with pressure and temperature to the same extent as the total volume does. Therefore, the quantitative composition of the gas mixture expressed in per cent does not depend on the temperature or pressure. It is only necessary to make sure that the temperature and pressure in the course of absorption are constant. This can usually be attained if the analysis is conducted in the shortest possible time.

PART THREE

ANALYSIS OF ORGANIC COMPOUNDS

CHAPTER XLII

Introduction

201. Methods of Organic Analysis

The analysis of organic compounds differs essentially from the analysis of inorganic compounds.

The greater part of inorganic substances is made up of electrolytes which in aqueous solution dissociate into ions and are determined as ions. Only a very few organic compounds ionize in aqueous solution. For the analysis of such substances the same methods are used as for the analysis of inorganic substances.

For example, organic acids are analysed by neutralization, i.e., by titration with alkali solutions in the presence of phenolphthalein indicator. The derivatives of carboxylic acids (anhydrides and acid chlorides) are converted to the respective acid which is then titrated with an alkali solution. Argentimetry is used for the analysis of halogen derivatives with replaceable halogen atoms (for example, benzyl chloride).

For the analysis of the majority of organic substances, however, use is made of characteristic reactions for each class of organic compounds, that are based on the specific chemical properties of the functional group contained in them. For instance, aldehydes, ketones and certain other groups contain the carbonyl group, $>C=O$, which is capable of reacting with hydroxylamine. This reaction is used for the quantitative determination of aldehydes and ketones.

For the analysis of aromatic amines (compounds containing the amino group, $-NH_2$) use is made of their reaction with sodium nitrite in an acidic solution (diazotization).

Thus, depending on the structure of the organic compound, various methods can be used for its determination.

Most of the methods for determining the composition of organic compounds considered in the following sections are methods of volumetric analysis similar to the methods of titrimetric analysis of inorganic substances, already described in Part Two.

Elementary quantitative and qualitative organic analysis is of major importance in research involving the synthesis of new compounds or the study of compounds of unknown structure. Qualitative analysis is used to determine what elements are present in an organic substance. Quantitative analysis is used to determine in what proportions the elements are contained in the substance.

Elementary quantitative analysis can be used, moreover, to estimate the quality of commercial organic products.

Commercial-grade products contain various impurities in addition to the basic substance and the primary purpose of industrial analytical laboratories is to determine the content of the basic substance and that of the impurities in them. In certain cases, prior to determining a certain constituent in a commercial product, it is necessary to remove other constituents that interfere with its determination.

The following sections will consider some of the common methods of analysis of organic compounds widely used in industrial and research laboratories.

CHAPTER XLIII

Elementary Qualitative Analysis

The majority of organic compounds are composed of a relatively small number of elements. The most important ones are: carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine.

Elementary qualitative analysis is concerned with the determination of the presence of individual elements in molecules of organic compounds.

202. Detection of Carbon and Hydrogen

On heating an organic substance in a gas flame it is charred and burned. Carbon is transformed to carbon dioxide; hydrogen, to water. If the substance under analysis is placed on a platinum plate which is carefully heated in the flame of a burner, charring indicates the presence of carbon.

A more precise method of simultaneously determining the presence of carbon and hydrogen is to heat a mixture of the organic compound and cupric oxide in a test tube with a gas-outlet tube. Secure the test tube in an almost horizontal position, immerse the end of the tube into a small beaker containing barium hydroxide solution. Carefully heat the contents of the test tube in a gas flame. If the substance under test contains hydrogen, drops of water will appear on the cold walls of the test tube. The appearance of suspended matter in the barium hydroxide solution indicates the presence of carbon in the substance under test.

203. Detection of Other Elements
Lassaigne's Test

To detect the presence of nitrogen, sulphur, and chlorine in an organic substance, the latter is decomposed so that the nitrogen, sulphur, and chlorine are converted to inorganic compounds which are then determined by standard procedures of qualitative analysis.

Fusion with alkali metals is used for decomposing the organic compound (Lassaigne's test).

As a result of the reaction of the organic substance with fused potassium at elevated temperatures, the nitrogen present in the organic substance forms potassium cyanide, KCN; sulphur is converted to potassium sulphide, K_2S; chlorine forms potassium chloride, KCl. If nitrogen and sulphur are present together in the substance under test, potassium thiocyanate, KCNS[1] may be formed.

[1] The processes that take place can be presented by the following schematic equations:

$$K + C + N = KCN$$
$$2K + S = K_2S$$
$$K + Cl = KCl$$
$$K + C + N + S = KCNS$$

Conduct the analysis as follows. Place a small portion of the organic substance (approx. 0.1 g) in a hard-glass test tube of small bore and add to it a piece of metallic potassium the size of a pea. Heat the test tube in a small flame, at first in the upper portion of the flame so that the potassium is melted and becomes fused with the substance under test. Then continue to heat until complete decomposition of the organic compound is achieved. This is usually accompanied by inflammation and charring of the substance. Immerse the test tube heated to red heat in a small beaker that contains 10-15 ml of cold water. On doing this the test tube cracks and its contents fall into the water. Any metallic potassium that has not reacted with the organic substance produces with water potassium hydroxide. In this case, inflammation may occur and therefore this operation should be carried out in a fume cupboard and the analyst should wear protective goggles.

Filter out the pieces of glass and particles of charcoal from the solution obtained above and test for the presence of nitrogen, sulphur, and chlorine in it. The solution is alkaline to litmus.

204. Detection of Nitrogen

To a portion of the filtered solution obtained above add one or two drops each of ferrous sulphate and ferric chloride solutions, mix, and heat for 1-2 minutes; then cool the solution and acidify with hydrochloric acid.

The appearance of a dark blue or green colour due to the conversion of potassium cyanide first to ferrous cyanide and then to potassium ferrocyanide indicates the presence of nitrogen in the compound under test:

$$2KCN + FeSO_4 = Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

Potassium ferrocyanide reacts with ferric chloride to form ferric ferrocyanide (Prussian blue):

$$3K_4[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12KCl$$

If the nitrogen content is large a dark blue precipitate of Prussian blue is formed.

205. Detection of Sulphur

Add a few drops of the above filtered solution to a freshly prepared solution of sodium nitroprusside, $Na_2[Fe(CN)_5 \cdot NO]$. The latter reacts with sulphide ions in alkaline solution to produce the complex $[Fe(CN)_5 \cdot NOS]^{4-}$ ion and the solution assumes a violet colour. The appearance of this colour indicates the presence of sulphur in the substance under test. The reaction with sodium nitroprusside is a very sensitive one and makes it possible to detect very small amounts of sulphur. If sulphur is present in large quantities, the solution turns from violet to blood-red.

Sulphur (to be more exact, sulphide ion) can be detected in the same solution by adding acetic acid and then lead acetate solution. The presence of sulphur is indicated by the appearance of a brown-black precipitate:

$$(CH_3COO)_2Pb + K_2S = 2CH_3COOK + PbS\downarrow$$

This test can also be carried out as follows: place 2-3 ml of the solution in a small test tube, add 1-2 ml of hydrochloric acid and heat.

Potassium sulphide is converted to hydrogen sulphide which is liberated from the solution on heating:

$$K_2S + 2HCl = 2KCl + H_2S\uparrow$$

The hydrogen sulphide liberated is detected by the blackening of lead-acetate paper held over the test tube.

$$(CH_3COO)_2Pb + H_2S = 2CH_3COOH + PbS$$

206. Detection of Chlorine

Acidify a portion of the filtered solution (obtained after decomposing the organic substance by the Lassaigne method) with nitric acid, heat to the boiling point, and add a few drops of silver nitrate solution to the hot solution. The formation of a white precipitate of silver chloride indicates the presence of chlorine in the substance under test:

$$AgNO_3 + KCl = KNO_3 + AgCl\downarrow$$

Heating with nitric acid is necessary to decompose any potassium cyanide and potassium sulphide which may have

formed if nitrogen and sulphur were present in the substance under test together with chlorine.

The Beilstein reaction is often used to detect chlorine (and other halogens). This reaction is based on the formation of volatile compounds on igniting chlorine-containing compounds with cupric oxide. The volatile products formed impart a green colour to the gas flame. Heat a copper wire in the gas flame until it no longer colours the flame, then touch it to the substance under test and insert it into the flame again. At first the organic material will burn, then the flame will be coloured green or a blue-green by the vapours of the copper chloride evolved. This is a very simple test and does not require preliminary decomposition by the Lassaigne method; it does not, however, always yield reliable results.

CHAPTER XLIV

Elementary Quantitative Analysis

Elementary quantitative organic analysis is used to determine the content of carbon, hydrogen, nitrogen, sulphur, chlorine and other elements in the molecule of an organic compound.

207. Quantitative Estimation of Carbon and Hydrogen

These elements are usually determined simultaneously by burning a weighed portion of the substance under test in a stream of air or oxygen in the presence of cupric oxide or platinum (as catalyst). Carbon is thus oxidised to carbon dioxide; hydrogen, to water. The carbon dioxide and water vapour formed, previously freed from other decomposition products, are carried away by the gas stream into absorption tubes.

The tube for absorbing water vapour is filled with anhydrone (magnesium perchlorate). The tube for absorption of carbon dioxide is filled with soda lime or ascarite (fused sodium hydroxide granulated with asbestos). Weigh the

absorption tubes before and after burning the weighed portion of the substance under test and calculate the content of carbon and hydrogen from the gain in weight of the respective tube.

The analysis is simplified if the substance contains only carbon, hydrogen, and oxygen. The oxygen content is calculated by difference.

If the substance contains, in addition, nitrogen, sulphur, and chlorine, it is necessary to remove the gaseous products formed on their combustion to prevent them from getting into the absorption tubes. Sulphur and chlorine are removed with the aid of lead chromate with which they react to form lead sulphate or lead chloride, respectively.

The oxides of nitrogen are removed by reducing them to gaseous nitrogen with metallic copper or converting them to lead nitrate with the aid of lead peroxide.

208. Quantitative Estimation of Nitrogen

Two methods are used to determine nitrogen in organic compounds: the *Kjeldahl method* and the *Dumas method.*

In the *Kjeldahl method* the substance under test is heated (digested) with concentrated sulphuric acid in the presence of a catalytic agent. The nitrogen is converted to ammonium sulphate, $(NH_4)_2SO_4$. Then an alkali is added to the reaction mixture. Ammonium sulphate decomposes and liberates ammonia:

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3\uparrow$$

The liberated ammonia is steamed out and titrated with an acid.

In the *Dumas method* the substance under test is heated with cupric oxide in an atmosphere of carbon dioxide. The nitrogen in the organic compound is transformed to gaseous nitrogen and oxides of nitrogen. The gaseous mixture is passed over red-hot copper in order to reduce the oxides of nitrogen and is then washed with an alkali solution. As a result, all the gaseous products are removed besides nitrogen, the volume of which is measured.

The Kjeldahl method is simpler and more convenient, especially for routine tests. It cannot, however, be used

for analyzing all nitrogen-containing organic compounds. For example, nitro, nitroso, and azo compounds must previously be reduced and then only decomposed by sulphuric acid. Sometimes the reducing agent (in particular, glucose) is added together with the sulphuric acid and both processes, reduction and decomposition, are carried out in one and the same flask.

Mercury or selenium are added to the sulphuric acid to speed up decomposition. The rate of decomposition is also increased at elevated temperatures. Sulphuric acid can be heated to 338°C; at this temperature it begins to boil. In order to carry out decomposition at higher temperatures, potassium sulphate is added to the sulphuric acid.

The Dumas method is suitable for analysis of all organic compounds. It requires, however, more complex apparatus and the procedure is considerably more complicated than in analysis by the Kjeldahl method.

The Dumas method is more frequently used in research laboratories. Industrial laboratories usually use the Kjeldahl method, especially for routine analyses.

209. Determination of Nitrogen by the Kjeldahl Method

Place a weighed portion of the substance under test in a round-bottomed flask with a long neck (Kjeldahl digestion flask) and add concentrated sulphuric acid and mercury or selenium. Secure the flask on a stand in a slightly inclined position and heat it gently, raising the temperature gradually. Then add anhydrous potassium sulphate and heat until a clear colourless solution is obtained. On the whole, digestion is continued from 2 to 3 hours. After cooling, transfer the solution quantitatively to a flask for distilling off ammonia. Rinse the Kjeldahl flask and its stopper with distilled water and carefully add the wash water to the main solution in the distillation flask.

After that add to the solution a little zinc dust and a few drops of phenolphthalein indicator. Close the distillation flask with a stopper that has two holes: in one of them insert a dropping funnel; in the other one, a tube for connecting the flask to the condenser and receiver (a flat-bot-

tomed conical flask provided with a special stopper carrying a tube filled with glass beads). Place an accurately measured quantity of 0.1*N* sulphuric acid in the receiver and connect it to the condenser. Prior to distilling, neutralize the solution in the distillation flask by adding from the dropping funnel sodium hydroxide until the solution is alkaline and then sodium sulphide solution. The latter, the same as the zinc dust, is added to decompose nitrogen compounds of mercury.

Gradually heat the contents of the distillation flask to the boiling point. The water vapour and ammonia produced pass through the condenser and are collected in the receiver. Continue distillation until a drop of the distillate from the condenser no longer has an alkaline reaction.

Titrate the contents of the receiver with an alkali solution and, from the quantity of free acid, calculate the nitrogen content in the substance under test.

210. Quantitative Estimation of Sulphur

The quantitative determination of sulphur in organic compounds is based on the oxidation of these compounds. On destruction of the compound, the sulphur contained in it is oxidized to SO_4^{2-} and is determined as sulphate ion.

Various oxidizing agents and conditions for oxidation are selected, depending on the properties of the organic compound and its resistance to oxidation.

Nonvolatile organic compounds containing large amounts of sulphur are oxidized by fusing them with potassium hydroxide and potassium nitrate in a silver evaporating dish heated on a gas burner. Fuse the solid potassium hydroxide with potassium nitrate in the dish. Cool, grind, and add a weighed portion of the substance under test; mix the mass and ignite it until it becomes white. Cool the fused cake, dissolve it in water, neutralize the excess of alkali with hydrochloric acid, and make the solution acidic to Congo paper. Precipitate SO_4^{2-} ions from this solution with barium chloride solution. Filter the precipitate of barium sulphate, wash it, dry it, and ignite to constant weight.

Simultaneously, conduct a blank test on a solution containing all the reagents except the substance under test.

Calculate the sulphur content from the formula

$$x = \frac{32\,(g_1 - g_2) \cdot 100}{233 \cdot 4 \cdot g}$$

where x = sulphur content, per cent;
g_1 = mass of the barium sulphate precipitated in the analysis, g;
g_2 = mass of the barium sulphate precipitated in the blank test, g;
g = weighed portion of the substance under test, g.

This method cannot be used to analyze volatile organic substances.

The content of sulphur in volatile organic compounds is determined by burning these substances with a mixture of sodium carbonate and potassium nitrate in a glass ignition tube sealed at one end. In the tube (in a horizontal position) place the oxidizing mixture (8 parts by weight of sodium carbonate and 1 part by weight of potassium nitrate), then the substance under test, and finally a layer of calcium carbonate to which potassium nitrate has been added. The calcium carbonate layer, filling more than half the length of the tube, prevents the volatile organic substances from escaping from the tube during ignition. First ignite the layer of calcium carbonate with the gas flame, then the substance under test. After ignition is completed, dissolve the contents of the tube in water, acidify, filter, and determine the content of sulphate ions in the filtrate by gravimetric analysis.

Another method of determining sulphur is based on oxidation of the organic substance with potassium permanganate in a medium of concentrated phosphoric acid. Conduct oxidation at a temperature of 120-140°C in a flask with a reflux condenser. When the reaction is over, decompose the excess of potassium permanganate with hydrogen peroxide, dissolve the contents of the flask in water, acidify with hydrochloric acid, and determine the content of sulphur ions by gravimetric analysis.

211. Determination of Chlorine and Sulphur by the Combustion Method

This method is based on the oxidation of the substance under analysis by burning a weighed portion in a flask filled with oxygen.

This analysis does not require complex apparatus and takes very little time to perform.

The sample should be burned in a 250-300 ml hard-glass flask provided with a ground-glass stopper. A platinum wire is soldered to the stopper; it should be of such a length that its end reaches the middle of the flask. The wire has a piece of platinum gauze at the end of it for holding the substance under test wrapped in quantitative (ashless) filter paper.

Pour into the flask a solution for absorbing the combustion products, fill the flask with oxygen from a gasometer or cylinder, ignite the edge of the filter paper, and quickly insert the stopper in the flask. The paper with the substance under test is burnt up and the combustion products are absorbed by the solution in the flask and then analyzed.

When determining the sulphur content, a hydrogen peroxide solution is used for absorbing the combustion products. On burning the sulphur and absorbing the combustion products, sulphur is converted to sulphate ions, which are determined by titrimetric analysis (for example, by titration with barium nitrate in the presence of thoron and methylene blue).

When determining the chlorine content, the combustion products are absorbed by an alkaline solution of hydrogen peroxide and the resulting sodium chloride is determined by the Volhard method.

In all cases a blank test should be conducted simultaneously, and if necessary, a correction made for the presence of sulphur or chlorine in the filter paper and reagents used in the test.

During combustion it is essential to press the stopper firmly in place so that it will not be forced out by the gases formed.

CHAPTER XLV

Bromometric Titrations

212. General Principles

Bromometric titrations are based on the ability of many organic compounds to react with bromine. If bromination is conducted under specified conditions, a definite number of bromine molecules will be substituted in or added to the molecule of the organic compound. Hence, the content of an organic compound in the sample under test can be calculated from the amount of bromine used in the titration.

This method is most frequently used for the analysis of unsaturated hydrocarbons, phenols, and amines.

213. Reaction of Unsaturated Hydrocarbons with Bromine

When compounds containing double bonds react with bromine, the latter is added at the double bond which is converted to a single bond. For example, one molecule of bromine is added to 1, 2-butane which is converted to 1, 2-dibromobutane:

$$CH_3 - CH_2 - CH = CH_2 + Br_2 \rightarrow CH_3 - CH_2 - CHBr - CH_2Br$$

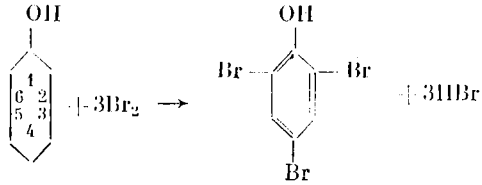
Two molecules of bromine are added to molecules of hydrocarbons that have two double bonds and the respective tetrabromoderivative is formed, for example,

$$CH_3 - CH = CH - CH_2 - CH_2 - CH = CH_2 + 2Br_2 \rightarrow$$
$$\rightarrow CH_3 - CHBr - CHBr - CH_2 - CH_2 - CHBr - CH_2Br$$

Thus, from the number of bromine molecules added it is possible to estimate the number of double bonds in the organic compound, i.e., the degree of unsaturation. The determination of the bromine number (or value), an important characteristic of many high-molecular organic compounds, is based on this principle. If the unsaturated compounds are present as impurities in compounds that do not react with bromine, the bromine number corresponds to the content of these impurities.

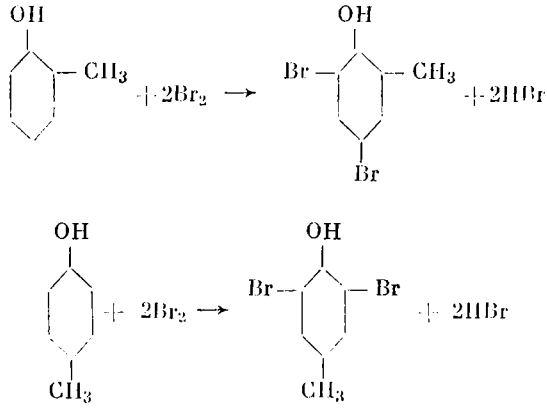
214. Reaction of Phenols with Bromine

Phenol reacts with bromine quantitatively at room temperatures. In contrast to the reaction with unsaturated hydrocarbons considered above, when phenol is brominated, hydrogen bromide is evolved. In this case substitution takes place, not addition, as in the previous cases. Bromine atoms replace three hydrogen atoms in the benzene ring of the phenol molecule—in positions *2*, *4*, and *6* relative to the hydroxyl group:

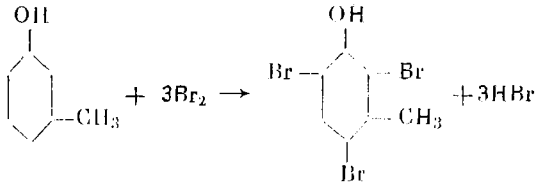


The homologues of phenol (for, example, the cresols) react in the same way as phenol does. In this case bromine also occupies the ortho- and para-positions relative to the hydroxyl group. If any of these positions are occupied by other substituents, a smaller number of bromine atoms will enter into the molecule.

Ortho- and para-cresol react with two bromine molecules:

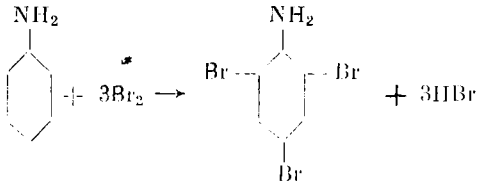


Meta-cresol reacts with three bromine molecules:



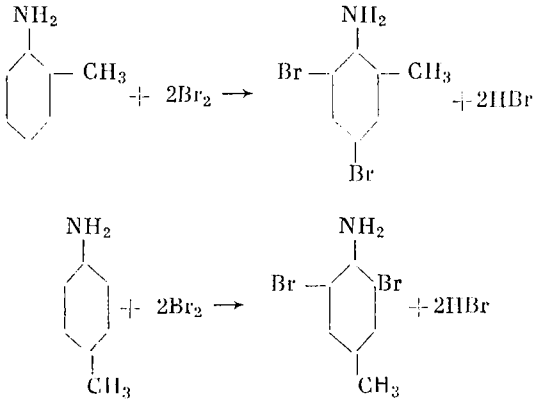
215. Reaction of Aromatic Amines with Bromine

On reacting with bromine, aniline is quantitatively transformed to 2,4,6-tribromaniline:

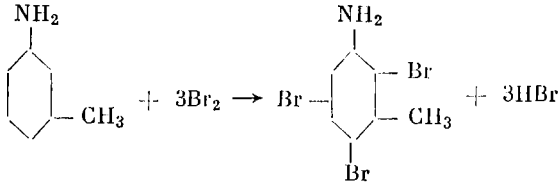


The aniline molecule, like the phenol molecule, reacts with three bromine molecules.

Ortho- and para-toluidine react with two bromine molecules to form dibromtoluidine:



Meta-toluidine reacts with three molecules of bromine to form tribromotoluidine:



Amines react with bromine more rapidly than phenols do. The rate of bromination is increased in the presence of potassium bromide.

216. Brominating Agents

Bromination is conducted by adding a bromine solution to the substance under test taken in the form of a solution or suspension. Bromine water, an aqueous solution of bromine, is not suitable for this purpose because of its ins ability on storage; moreover, most organic compounds are insoluble in water, which makes brominating with bromine water difficult.

Occasionally use is made of a solution of bromine in organic solvents, such as carbon tetrachloride or alcohol saturated with sodium bromide. These solutions are prepared with bromine, a substance that is very toxic and demands great care in handling. On contact with the skin it may cause bad burns; its vapours are poisonous and have a destructive effect on the respiratory tract and eyes.

It is much more convenient to use a mixture of potassium bromide, KBr, and potassium bromate, $KBrO_3$. Under specific conditions bromine is liberated from a solution containing potassium bromide and potassium bromate as follows:

$$5KBr + KBrO_3 + 6HCl = 3Br_2 + 6KCl + 3H_2O$$

$$5 \mid Br^- - e \rightarrow Br$$

$$1 \mid BrO_3^- + 6H^+ + 5e \rightarrow Br + 3H_2O$$

Thus, one molecule of potassium bromate oxidizes five molecules of potassium bromide. This reaction takes place

only in acidic solution. A neutral aqueous solution of potassium bromide and potassium bromate can stand for a long time without liberating bromine. However, on adding an acid to it or pouring it into a solution containing an acid, the oxidation-reduction reaction immediately ensues and bromine is liberated in a quantity equivalent to that of the potassium bromate in the solution.

An aqueous solution containing potassium bromide and potassium bromate, usually called bromate-bromide solution, is widely used in analysis by titration with bromine.

217. Bromometric Titration Procedures

Two methods of titration are used in analysis by bromination: direct and back titration.

Direct titration is used for the analysis of compounds which are rapidly brominated. It is carried out as follows. Dissolve the sample in a suitable solvent and titrate with a standard solution (usually a bromate-bromide solution). As titration proceeds, bromine reacts with the compound under test. When the chemical reaction between bromine and the organic compound is just completed, free bromine appears in the solution under test on adding a new portion of the bromate-bromide solution to it. Bromine is detected with the aid of starch-iodide paper (ash-free filter paper moistened with an aqueous solution of starch and potassium iodide). The change in colour of the starch-iodide paper is due to the reaction of bromine with the potassium iodide contained in it, which is oxidized to free iodine:

$$Br_2 + 2KI = I_2 + 2KBr$$

The liberated iodine turns the starch-iodide paper blue (for a more detailed description of the preparation and properties of starch-iodide paper see Sec. 224).

Direct titration is usually used for the analysis of amino compounds.

This method is not suitable for the analysis of compounds that are brominated slowly. In this case, to attain complete bromination, use is made of back titration which is carried out as follows. To the solution under test add the bromate-

bromide solution in a quantity that exceeds the amount needed for bromination. After some time has expired, determine the excess of bromine (that has not entered into reaction) by iodometry. For this purpose, add potassium iodide solution to the solution under test. In acidic solution, potassium iodide reacts quantitatively with the excess of bromine, liberating iodine in a quantity equivalent to the excess of bromine. Titrate the iodine with thiosulphate solution. This method is usually employed for the analysis of phenols.

Unsaturated hydrocarbons are analyzed by means of back titration, using solutions of bromine in organic solvents.

218. Preparation of Bromate-Bromide Solution

On adding acid to the bromate-bromide solution, each gram-molecule of potassium bromate yields 3 moles or 6 gram-equivalents of bromine:

$$5KBr + KBrO_3 + 6HCl = 3Br_2 + 6KCl + 3H_2O$$

Therefore, the gram-equivalent of potassium bromate is equal to mole/6:

$$E_{KBrO_3} = \frac{M_{KBrO_3}}{6} = \frac{167.02}{6} = 27.84$$

When preparing the standard bromate-bromide solution, the amount of potassium bromide taken considerably exceeds the stoichiometric proportion in which it reacts with potassium bromate. An excess of potassium bromide, in many cases, accelerates bromination.

The titre of the bromate-bromide solution is determined by the potassium bromate content. Usually a 0.5 or a 0.1*N* solution is used.

To prepare 0.5*N* solution, dissolve 13.92 g of potassium bromate in distilled water, add 60 g of potassium bromide, mix, and after the salts have dissolved, make up to 1 litre with distilled water in a measuring flask.

219. Standardization of Bromate-Bromide Solution

The bromate-bromide solution is standardized by iodometry. For this purpose mix an accurately measured quantity of the above solution with potassium iodide solution and acidify with sulphuric acid. The bromine liberated oxidizes the iodide ion to free iodine:

$$2KI + Br_2 = 2KBr + I_2$$

Iodine is liberated in an amount equivalent to the quantity of bromine and is titrated with thiosulphate solution, using starch solution as indicator:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

Thus, the amount of thiosulphate used in the titration is equivalent to the amount of bromine liberated. If the concentration of the thiosulphate solution is known, the concentration of the bromate-bromide solution can be calculated from the formula

$$N_x = \frac{N \cdot a}{V_x}$$

where N_x = concentration of bromate-bromide solution, g-equiv/lit;
V_x = volume of bromate-bromide solution taken for titration, ml;
N = concentration of thiosulphate solution, g-equiv/lit;
a = volume of thiosulphate solution used in the titration, ml.

Example. After 50 ml of approximately 0.5N bromate-bromide solution were poured into a 250-ml measuring flask, the solution was made up to the mark with water and 25 ml of the resulting solution were transferred to a conical flask with a ground-glass stopper. Then 25 ml of 10 per cent potassium iodide solution were added to the flask, the mixture stirred, and 20 ml of 20 per cent sulphuric acid added, the flask stoppered tightly and put in a dark place for 5 minutes. The iodine liberated was then titrated with 0.1N thiosulphate solution, using starch as the indicator.

Suppose 24.20 ml of thiosulphate solution were used in the titration.

The concentration of the bromate-bromide solution is calculated from the formula

$$N_x = \frac{0.1 \times 24.20 \times 250}{50 \times 25} = 0.484 \text{ g-equiv/lit}$$

220. Analysis of Commercial Aniline

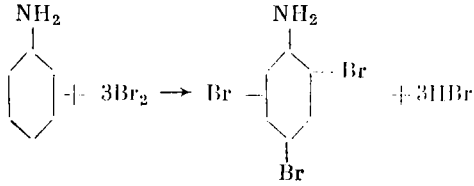
Aniline, like other aromatic amines, is a compound that is rapidly brominated; therefore, direct bromometric titration is used in its analysis.

Prior to conducting the analysis, dry a sample of the commercial aniline with calcined calcium sulphate. Then dissolve an accurately weighed portion of the dried aniline in hydrochloric acid, transfer the solution to a measuring flask and make up to the mark with distilled water. Introduce into a titration beaker provided with a glass stirring rod an accurately measured (pipetted) volume of the aniline solution, and add potassium bromide solution and hydrochloric acid. The potassium bromide accelerates bromination of the aniline. A high rate of bromination is essential for direct bromometric titration.

Titrate the contents of the beaker with the bromate-bromide solution, stirring constantly. On adding a portion of the bromate-bromide solution to the solution under test, bromine is immediately liberated and begins to react with the aniline at once. In the process of titration, wet the end of the stirring rod with the solution in the beaker and touch it to starch-iodide paper. As long as there is any aniline in the solution, the bromine liberated continues to react with it, and the colour of the starch-iodide paper does not change. The moment bromination of aniline is completed, free bromine will appear in the solution on adding the following portion of the bromate-bromide solution, and a dark spot will form on starch-iodide paper.

In this analysis, the indicator is not added to the titrated solution. Such a procedure is called titration with an *external indicator*.

The aniline content is calculated on the basis of the reaction equation



according to which 6 gram-equivalents of bromine are used for brominating 1 mole of aniline.

Therefore, the gram-equivalent of aniline in this reaction is equal to $^1/_6$ its molecular weight, i.e., 93.13 : 6 = 15.52.

The aniline content in per cent is calculated from the formula

$$x = \frac{15.52 \cdot N \cdot a \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where

x = aniline content in the commercial product, per cent;
N = concentration of the bromate-bromide solution, g-equiv/lit;
a = volume of the bromate-bromide solution used in the titration, ml;
V_f = capacity of the measuring flask, ml;
V_p = capacity of the pipette, ml;
g = weighed portion of commercial aniline, g.

Example. A portion of aniline weighing exactly 9.9006 g was dissolved in 30 ml of 10 per cent hydrochloric acid, transferred to a 1000-ml measuring flask and made up to the mark with distilled water. From the measuring flask, 25 ml of the aniline solution were poured into a titration beaker containing 200 ml of 10 per cent potassium bromide solution and 20 ml of concentrated hydrochloric acid. The mixture was then titrated with 0.5 N bromate-bromide solution until a dark spot appeared on the starch-iodide paper.

Suppose that 31.88 ml of bromate-bromide solution were used in the titration.

The content of aniline in the commercial product was

$$x = \frac{15.52 \times 0.5 \times 31.88 \times 1000 \times 100}{1000 \times 9.9006 \times 25} = 99.95\%$$

221. Analysis of Commercial Phenol

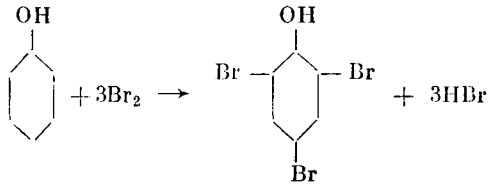
Phenol is brominated much more slowly than aniline and, therefore, back titration is used for its analysis which is carried out as follows. Dissolve an accurately weighed portion of the phenol in water and make up to the mark in a measuring flask with water.

Bromination is conducted in a special flask with a ground-glass stopper in which a dropping funnel is sealed. Transfer an accurately measured volume of the diluted phenol solution to the flask with the aid of a pipette, and add an accurately measured volume of the bromate-bromide solution from a burette. The latter solution is taken in excess relative to the quantity required for bromination. After that, close the flask tightly with the stopper carrying the dropping funnel, and slightly opening the stopcock of the funnel, connect the neck of the funnel with a suction pump for a short time. Then close the stopcock of the funnel, disconnect it from the suction pump, and pour hydrochloric acid into the funnel. A small vacuum is maintained in the flask. Carefully open the stopcock and slowly discharge the acid into the flask. Close the stopcock while there is still some acid in the funnel. In this way a vacuum is maintained in the flask, which prevents the escape of bromine vapours liberated when the brominating reaction begins on adding the acid. After adding the acid, stir the contents of the flask and allow it to stand for some time so that bromination takes place quantitatively. Part of the bromine equivalent to the quantity of phenol contained in the solution will react with the latter and the excess of bromine will remain in the solution. To determine the excess of bromine, add potassium iodide solution into the flask through the dropping funnel, leaving 2-3 ml of liquid in it. This liquid plays the role of a hydraulic seal and keeps the bromine vapours from escaping.

The potassium iodide added reacts with the excess of bromine, and iodine is liberated equivalently. Shake the contents of the flask so that the bromine vapours are completely absorbed, dispense with the vacuum, remove the stopper with the dropping funnel, and titrate with thiosulphate solution in the presence of starch solution.

Since iodine is formed in a quantity equivalent to the quantity of free bromine, the bromine content can be calculated from the amount of thiosulphate used in the titration.

Three moles, i.e., 6 gram-equivalents, of bromine react with 1 mole of phenol:



Hence, the gram-equivalent of phenol in this reaction is equal to $^1/_6$ of its molecular weight, i.e., 94.11 : 6 = 15.68.

The phenol content in the commercial product is calculated from the formula

$$x = \frac{15.68\,(N \cdot a - N_1 \cdot b) \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where x = content of phenol in the commercial product, per cent;

N = concentration of bromate-bromide solution, g-equiv/lit;

a = volume of the bromate-bromide solution added to the solution under test, ml;

N_1 = concentration of thiosulphate solution, g-equiv/lit;

b = volume of thiosulphate solution used in the titration, ml;

V_f = capacity of the flask, ml;

V_p = capacity of the pipette, ml;

g = weighed portion of the commercial product, g.

Example. After 2.3520 g of commercial phenol were dissolved in 100 ml of distilled water, the resulting solution was transferred quantitatively to a 1000-ml measuring flask and made up to the mark with distilled water.

Ten ml of the diluted phenol solution and 50 ml of 0.1*N* bromate-bromide solution were introduced into the bromination flask which was then closed with a ground-glass stopper

carrying a dropping funnel. A vacuum was created in the flask and about 20 ml of 10 per cent hydrochloric acid were added into it. The contents of the flask were shaken up and then allowed to stand for 20 minutes. After that 20 ml of 10 per cent potassium iodide solution were added through the funnel, the mixture stirred, 0.3 ml of 1 per cent starch solution added and the liberated iodine titrated with 0.1*N* thiosulphate solution.

Suppose that 35.80 ml of thiosulphate solution were used in the titration.

The content of phenol in the commercial product was

$$x = \frac{15.68 \times (0.1 \times 50 - 0.1 \times 35.80) \times 1000 \times 100}{1000 \times 2.3520 \times 10} = 94.66\%$$

222. Determination of Bromine Number in Commercial Benzene

Commercial benzene is contaminated with unsaturated hydrocarbons. To determine the content of these impurities, the sample of commercial benzene is treated with excess bromate-bromide solution in the presence of an acid.

The unsaturated hydrocarbons are thus brominated and the excess of bromine is determined by iodometric analysis. Since the content of unsaturated hydrocarbons in benzene is small, the volumes of the solutions added are also small and 2- or 5-ml microburettes are used for this analysis.

The content of unsaturated hydrocarbons is expressed as the bromine number, i.e., the number of grams of bromine used in the reaction with 100 ml of benzene.

The bromine number is calculated from the formula

$$x = \frac{80\,(aN - bN_1) \cdot 100}{1000 \cdot V}$$

where x — the bromine number, g per 100 ml;
a — the volume of the bromate-bromide solution added to the solution under test, ml;
N — concentration of the bromate-bromide solution, g-equiv/lit;
b — volume of the thiosulphate solution used in the titration, ml;

N_1 = concentration of the thiosulphate solution, g-equiv/lit;
V = volume of benzene taken for analysis, ml;
80 = atomic weight of bromine (rounded off).

This is the quantity of bromine liberated by 1 litre of $1N$ bromate-bromide solution.

In routine tests it is convenient to use exactly $0.1N$ bromate-bromide and thiosulphate solutions. The formula used for calculating the bromine number will then be

$$x = \frac{(a-b)\cdot 0.8}{V}$$

Example. In a flask with a ground-glass stopper were placed 10 ml of 25 per cent sulphuric acid solution, exactly 5 ml of commercial benzene were pipetted into the flask, and 1 ml of $0.1N$ bromate-bromide solution was added from a microburette. After that the flask was tightly stoppered, wrapped in a piece of dark cloth to protect it against daylight, shaken up for 5 minutes, and then allowed to stand for 1 minute.

The contents of the flask separated into layers; the top layer consisting of hydrocarbons became yellow in colour. Two ml of 25 per cent potassium iodide were added to the flask, the mixture shaken up, and the liberated iodine titrated with $0.1N$ thiosulphate solution from a microburette.

Suppose that 0.25 ml of thiosulphate solution was used in the titration.

The bromine number of the commercial benzene under test was

$$x = \frac{(1.00-0.25)\cdot 0.8}{5} = 0.12 \text{ g per } 100 \text{ ml}$$

CHAPTER XLVI

Diazotization Method

223. General Principles

Diazotization is employed in the analysis of aromatic compounds containing an amino group in their molecule. This analysis is based on the reaction between the aromatic amine and nitrous acid in the presence of excess inorganic

acid. The reaction proceeds in several steps and terminates in the formation of a diazo compound.

Sodium nitrite is usually used in the direct method of diazotization; it yields nitrous acid in acidic solutions. If portions of sodium nitrite solution are added to a solution containing aniline and hydrochloric acid, the sodium nitrite is gradually converted to nitrous acid which then forms with the aniline the diazo compound, phenyl diazonium chloride.

The overall equation for the reaction is

$$C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2Cl + NaCl + 2H_2O$$

When all of the aniline has reacted with the sodium nitrite, the next portion of sodium nitrite added to the solution under test is converted to nitrous acid which remains in the solution and can be detected with the aid of starch-iodide paper.

Thus, the appearance of free nitrous acid in the solution under test indicates that the diazotization reaction is completed and the equivalence point attained.

In titration with sodium nitrite, use is made of an external indicator: in the course of titration, wet the end of a stirring rod with the solution being titrated and touch it to a strip of starch-iodide paper. The appearance of a blue spot indicates that the equivalence point has been reached.

Diazotization proceeds quantitatively only in the presence of an inorganic acid. For this reason the acidity of the solution is checked with Congo paper before and during titration. It is particularly important to check the acidity at the end of titration; if there is no excess of acid present, the starch-iodide paper will not detect excess sodium nitrite and, therefore, will not indicate the end-point of titration.

224. Determination of the End-Point of Titration

Starch-iodide paper is used as the indicator for determining the end-point of titration in the diazotization test. The paper is prepared as follows: moisten ash-free filter paper with an aqueous solution of starch and potassium iodide (10 g of soluble starch and 2 g of potassium iodide

per 1 litre of water); then dry the paper in a dark place and keep it in a dark-coloured glass jar.

Starch-iodide paper is used for detecting the presence of oxidizing agents (for instance, bromine in direct bromometric titration), but it is mainly used to detect excess sodium nitrite in the diazotization reaction (hence, it is also known as 'nitrite paper').

Nitrous acid reacts with the potassium iodide contained in the starch-iodide paper, oxidizing it and liberating iodine which turns the starch-iodide paper blue.

The sensitivity of starch-iodide paper depends largely on the way it is prepared and on the grade of the filter paper used.

At the equivalence point the solution under test contains a very small amount of nitrous acid. A drop of such a solution may not cause a dark spot to appear on the starch-iodide paper because of the low concentration of nitrous acid in it.

Therefore, the spot does not appear at the equivalence point, but somewhat later, when an excess of the nitrite solution is added. This excess can be considerable and thus lead to erroneous test results which, however, can be avoided by introducing a correction for the sensitivity of the starch-iodide paper.

For this purpose, carry out a blank test, i.e., titrate a solution that contains the same quantity of water and acid as the solution under test, but does not contain the amino compound under test. Continue titration until a spot similar to the one obtained on titrating the solution of the amino compound appears. The amount of the nitrite solution used in the blank titration is the correction for the sensitivity of the starch-iodide paper. It can be as great as 0.1-0.2 ml and must be subtracted from the volume of the nitrite solution used in the titration of the solution under test.

225. Conditions for Diazotization of Different Amines

Depending on the properties of the analyzed amine, the conditions of titration may vary, although the procedure remains the same. The most important of these conditions

are the rate of titration and temperature of the solution under test.

Rate of titration. Different amino compounds react with nitrous acid at different rates; titration is conducted, therefore, so that the nitrite added has time to change to nitrous acid and enter into reaction with the amine without accumulating in the solution under test.

Amines are classified as rapidly or slowly diazotizable, depending on the rate of conversion into diazo compounds. Rapidly diazotizable amino compounds include compounds that contain, besides the amino group, the sulpho group, nitro group, or carboxyl group in the aromatic ring. Such compounds are, for instance, isomeric nitroanilines, as well as metanilic, sulphanilic, and anthranilic acids.

Slowly diazotizable compounds are those that do not contain any substituent group other than the amino group or that contain, in addition to the latter, the methyl or hydroxyl group. Such compounds include aniline, the isomeric aminophenols, toluidines. The rate of diazotization can be appreciably increased by adding potassium bromide to the solution under test containing an amine and an inorganic acid. Slowly diazotizable compounds are usually titrated in the presence of potassium bromide.

Of great significance in determining the end-point of titration precisely is the time it is necessary to wait after adding the last portion of sodium nitrite. For amines that are diazotized slowly, the solution under test should be allowed to stand from 5 to 10 minutes in order to give the last portion of the nitrite solution sufficient time to react fully with the amine.

For amines that are rapidly diazotized, the solution is allowed to stand from 30 seconds to 2 minutes.

Only after the specified time has elapsed can the test for the end-point of titration be made. If it is made immediately after titrating, an error is inevitably introduced: the nitrous acid that has not yet entered into reaction with the amine will be taken for excess acid, indicating that the equivalence point has already been reached.

Industrial procedures for analyzing particular amines always specify the time the solution should be allowed to stand after titration is completed.

Effect of temperature. The diazo compounds that are formed on diazotization of amines are unstable and readily decomposed at elevated temperatures. Decomposition of the diazo compounds in the course of the titration can lead to side (secondary) reactions and give erroneous test results.

To eliminate the possibility of decomposition of the diazo compound, titration is carried out at low temperatures. The solution under test is cooled by placing the beaker containing it in a bath with a cooling mixture or by adding cracked ice into the solution.

The most favourable temperature for titrating different amines varies with the stability of the diazo compound formed. Amines that form relatively stable diazo compounds are titrated at a temperature of 15-20°C. Aniline, ortho- and paratoluidine, para-aminophenol, benzidine, and other compounds are titrated at this temperature.

Amines that form unstable diazo compounds are titrated at a temperature of 0-5°C. Such amines include metatoluidine, α-naphthylamine, para-aminoacetanilide, and several other compounds.

Amines that contain, in the aromatic ring, the sulpho group in addition to the amino group form the most stable diazo compounds. Such amines are titrated at a temperature of 20-40°C.

226. Preparation of Standard Sodium Nitrite Solution

Usually 0.1*N* or 0.5*N* sodium nitrite solution is used for the titration.

One molecule of sodium nitrite reacts with one amino group and, consequently, the gram-equivalent of sodium nitrite in this reaction is numerically equal to its molecular weight.

To prepare a 0.5*N* solution, dissolve 34.5 g of crystalline sodium nitrite (analytically pure or chemically pure) and make the solution up to the mark in a 500-ml measuring flask.

Standardize the nitrite solution against sulphanilic acid (4-aminobenzenesulphonic acid). Pure sulphanilic acid suitable for standardization is usually obtained from the com-

mercial sodium salt. This salt is recrystallized several times from boiling water to which active carbon has been added. After recrystallizing three times in succession, filter out the crystals, dissolve them in distilled water, and add hydrochloric acid until the solution is acidic to Congo paper. The stronger hydrochloric acid displaces the sulphanilic acid from the solution of its salt and sulphanilic acid is precipitated. Filter out the precipitate, wash it with cold water, and recrystallize two or three times from boiling water. Dry the sulphanilic acid thus purified in a drying cabinet at 110°C to constant weight and keep it in a jar with a ground-glass stopper.

Sulphanilic acid is sparingly soluble in water (at 20°C approximately 1 g dissolves in 100 g of water). To prepare the solution used for standardization, dissolve an accurately weighed portion of the sulphanilic acid (about 2.5 g) in 100-150 ml of water, adding a small amount of sodium hydroxide or ammonia to attain complete dissolution. Transfer the solution prepared in this way to a titration beaker, make up to a volume of 400-500 ml with water, acidify with hydrochloric acid, and titrate at 20°C with the nitrite solution.

Make the test with starch-iodide paper 2 minutes after titration is completed.

Simultaneously, conduct a blank test for determining the correction for the sensitivity of the starch-iodide paper.

The normality of the standard sodium nitrite solution is calculated from the formula

$$N = \frac{1000 \cdot g}{173.2\,(a - a_1)}$$

where N = concentration of the sodium nitrite solution, g-equiv/lit;

g = weighed portion of sulphanilic acid, g;

a = volume of sodium nitrite solution used in the titration, ml;

a_1 = volume of sodium nitrite solution used in the titration in the blank test, ml;

173.2 = gram-equivalent of sulphanilic acid

Example. $g = 2.5200$ g; $a = 28.62$ ml; $a_1 = 0.22$ ml;

$$N = \frac{1000 \times 2.5200}{173.2\,(28.62 - 0.22)} = 0.512 \text{ g-equiv/lit}$$

227. Determination of Aniline Hydrochloride in the Commercial Product

Aromatic amines, as a rule, are not soluble in water; therefore, for their analysis, they are dissolved in an aqueous solution of an acid.

Aniline hydrochloride, $C_6H_5NH_2 \cdot HCl$, dissolves in water without the addition of an acid.

Dissolve a weighed portion of aniline hydrochloride in distilled water, make the volume up to the mark in a measuring flask with distilled water, and with the aid of a pipette, transfer an accurately measured volume of the resulting solution to the titration beaker. Prior to titrating, add hydrochloric acid and potassium bromide solution to the solution under test.

The diazobenzene formed on diazotization is a comparatively stable compound, therefore, titration is conducted at a temperature of 15-20°C. The presence of free acid is checked by Congo paper several times in the course of the titration. If the indicator shows that acid is absent, immediately add hydrochloric acid until the solution is clearly acidic to Congo paper.

Towards the end of titration, add the nitrite solution a drop at a time and after adding each successive drop, determine whether the equivalence point (the end-point of diazotization) has been reached. Proceed as follows: wet the end of a stirring rod with the solution and touch it to a strip of starch-iodide paper. Titration is considered to be complete if a drop of the solution, taken 10 minutes after adding the last portion of nitrite solution, colours the starch-iodide paper.

Simultaneously, carry out a blank test to determine the correction for the sensitivity of the starch-iodide paper.

The content of aniline hydrochloride in the commercial product is calculated from the formula

$$x = \frac{129.6 \cdot N \cdot (a - a_1) \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where x = content of aniline hydrochloride, per cent;
N = concentration of the sodium nitrite solution, g-equiv/lit;

a = volume of sodium nitrite solution used in the titration, ml;
a_1 = volume of sodium nitrite solution used in the titration in the blank test, ml;
V_f = capacity of the measuring flask, ml;
V_p = capacity of the pipette, ml;
g = weighed portion of aniline hydrochloride, g;
129.6 = gram-equivalent of aniline hydrochloride.

Example. A portion of aniline hydrochloride weighing 9.5010 g was dissolved in distilled water, quantitatively transferred to a 250-ml measuring flask, and the solution made up to the mark with distilled water. Into a titration beaker were pipetted 50 ml of the solution and 10 ml of distilled water, 30 ml of 10 per cent hydrochloric acid solution, and 20 ml of 10 per cent potassium bromide solution were added, and the resulting solution was titrated with 0.5N sodium nitrite solution.

Suppose that 28.80 ml of the sodium nitrite solution were used in the titration and 0.20 ml of the sodium nitrite solution was used in the titration in the blank test.

The content of aniline hydrochloride was

$$x = \frac{129.6 \times 0.5 (28.80 - 0.20) \times 250 \times 100}{1000 \times 9.5010 \times 50} = 97.55\%$$

228. Analysis of *p*-Nitroaniline

Unlike aniline, paranitroaniline is sparingly soluble in dilute hydrochloric acid. It is dissolved on heating in an excess of concentrated hydrochloric acid.

The nitro ($-NO_2$) group contained in the paranitroaniline molecule also effects the rate at which it reacts with nitrous acid. Paranitroaniline is diazotized very rapidly and there is no need of adding potassium bromide to the solution prior to titrating. The sodium nitrite solution is added quickly and the solution under test is allowed to stand not longer than 30 seconds at the end of diazotization. Titration is conducted at a temperature of 7-10°C which is maintained by adding cracked ice to the solution under test.

The paranitroaniline content is calculated from the formula

$$x = \frac{138.13\,(a - a_1) \cdot N \cdot 100}{1000 \cdot g}$$

where x = content of paranitroaniline, per cent;
a = volume of sodium nitrite solution used in the titration, ml;
a_1 = volume of sodium nitrite solution used in the titration in the blank test, ml;
N = concentration of the sodium nitrite solution, g-equiv/lit;
g = weighed portion of paranitroaniline, g;
138.13 = gram-equivalent of paranitroaniline.

Example. A portion of paranitroaniline weighing 2.7626 g was transferred quantitatively to a titration beaker, 50 ml of concentrated hydrochloric acid and 40 ml of distilled water were added, and the resulting solution was heated until the paranitroaniline was completely dissolved. The solution was then cooled, diluted with 250 ml of distilled water and ice was added to cool the solution to 7°C. At this temperature the paranitroaniline was titrated with 0.5N sodium nitrite solution. A blank test was conducted simultaneously.

Suppose that 37.65 ml of the sodium nitrite solution was used in the titration and 0.15 ml of the sodium nitrite solution was used in the titration in the blank test.

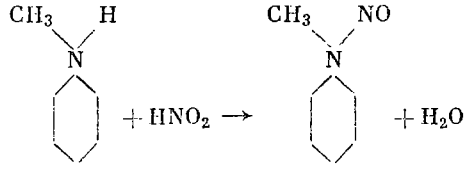
The content of paranitroaniline in the commercial product was

$$x = \frac{138.13\,(37.65 - 0.15) \times 0.5 \times 100}{1000 \times 2.7626} = 93.75\%$$

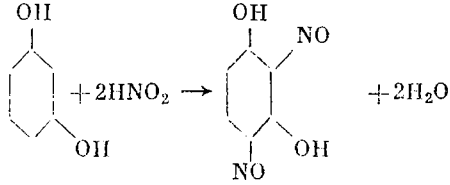
229. Principles of the Nitrosation Method

Nitrous acid reacts quantitatively not only with primary aromatic amines but, likewise, with certain other organic compounds as, for instance, secondary aromatic amines, phenols, and naphthols. Nitroso compounds are formed as a result of the reaction of these compounds with nitrous acid. Secondary amines form N-nitrosamine, compounds in which the nitroso group is bound to the nitrogen in the

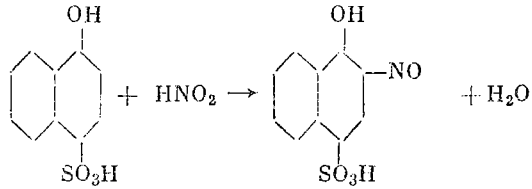
amino group. For example, monomethylaniline is quantitatively converted to N-nitrosomethylaniline:



Resorcinol reacts with two molecules of nitrous acid to form the corresponding nitroso compound:



1-naphthol-4-sulphonic acid reacts with one molecule of nitrous acid to form 2-nitroso-1-naphthol-4-sulphonic acid:

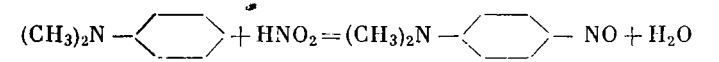


The procedure followed in nitrosation is the same as that used in diazotization. In this test a standard sodium nitrite solution is also used in the titration. Hydrochloric acid is added to the solution of the compound under test and then the standard sodium nitrite solution is added in portions from a burette. As the sodium nitrite solution is introduced into the solution under test, nitrous acid is formed, which reacts with the compound being analyzed to form the corresponding nitroso derivative. When nitrosation is completed, an additional drop of the sodium nitrite solution produces free nitrous acid in the solution under test; the nitrous acid is detected with the aid of starch-iodide paper. The content of the analyzed compound is

determined from the amount of sodium nitrite solution used in the titration. Thus, the method of determining the equivalence point is the same as in the diazotization method. A blank test is carried out simultaneously with the analysis to determine the correction for the sensitivity of the starch-iodide paper.

Nitrosation of different compounds proceeds at different rates and, therefore, individual compounds can be determined without separating them from the mixture. For example, in a dilute aqueous solution, nitrosation of resorcinol takes place quantitatively, whereas nitrosation of phenol is practically absent. This makes it possible to conduct the quantitative determination of resorcinol in the presence of phenol.

Tertiary amines (for example, dimethylaniline) react with nitrous acid very slowly to form paranitroso derivatives:



This reaction practically does not take place in dilute solutions; therefore, secondary amines can be determined in the presence of tertiary amines.

The rate of nitrosation of amines is enhanced in the presence of potassium bromide.

Many of the nitroso compounds formed in the course of the analysis are chemically active; when these products are subject to side reactions that can give erroneous results, nitrosation is conducted after cooling the solution under test to the appropriate temperature.

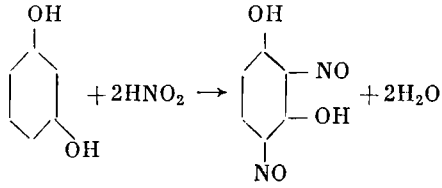
230. Determination of Resorcinol in the Commercial Product

As resorcinol is readily soluble, dissolve the weighed portion taken for the analysis in distilled water directly in a measuring flask and make the solution up to the mark with distilled water. Transfer an accurately measured volume of the solution with a pipette to the titration beaker and add hydrochloric acid and water to it. In nitrosation of resorcinol it is necessary to dilute the solution conside-

rably in order to avoid nitrosation of phenol which may be present as an impurity in commercial resorcinol.

Heat the beaker with the solution gently in a water bath, and titrate at 30-35°C with sodium nitrite solution. After titrating, allow the solution to stand for 15 minutes. Simultaneously, conduct a blank test.

One molecule of resorcinol reacts with two molecules of nitrous acid to form 2, 4-dinitroso resorcinol:



Therefore, a gram-equivalent of resorcinol in this reaction is equal to $^1/_2$ of its molecular weight, i.e., 110.11 : 2 = = 55.05.

The content of resorcinol in the product under test is calculated from the formula

$$x = \frac{55.05\,(a - a_1) \cdot N \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where x = content of resorcinol in the product under test, per cent;

a = volume of sodium nitrite solution used in the titration, ml;

a_1 = volume of sodium nitrite used in the blank test, ml;

N = concentration of sodium nitrite solution, g-equiv/lit;

V_f = capacity of the measuring flask, ml;

V_p = capacity of the pipette, ml;

g = weighed portion of the commercial product, g.

Example. A portion of resorcinol weighing 2.7525 g was transferred quantitatively to a 250-ml measuring flask, dissolved in distilled water, and the solution made up to the mark with water. By means of a pipette 50 ml of the resorcinol solution was transferred to a titration beaker, 70 ml of 10 per cent hydrochloric acid and 500 ml of water were added and the resulting solution was heated to 30°C

and then titrated with 0.5*N* sodium nitrite solution. In the blank test, 50 ml of distilled water was taken instead of the resorcinol solution.

Suppose that 19.95 ml of sodium nitrite solution were used in the titration and 0.12 ml of sodium nitrite solution was used in the titration in the blank test.

The content of resorcinol in the commercial product was

$$x = \frac{55.05\,(19.95 - 0.12) \times 0.5 \times 250 \times 100}{1000 \times 2.7525 \times 50} = 99.15\%$$

CHAPTER XLVII

Reductimetric Method

231. General Principles

The reductimetric method is used for the quantitative analysis of compounds that contain the nitro group ($-NO_2$), nitroso group ($-NO$), azo group ($-N=N-$), or hydrazo group ($-HN-NH-$). It is based on the ability of these compounds to be reduced quantitatively to amines by the action of reducing agents.

$$RNO_2 \rightarrow RNH_2$$

$$RNO \rightarrow RNH_2$$

$$R-N=N-R \rightarrow 2RNH_2$$

$$R-NH-NH-R \rightarrow 2RNH_2$$

The content of the substance under test is determined either by the amount of amino compound formed or by the amount of reducing agent that enters into reaction.

When the content is determined by the amount of reducing agent used in the reaction, it is imperative that the conditions of reduction be strictly observed. Any departure from them can lead to side reactions as a result of which the amount of reducing agent used will be much less than the theoretical quantity.

When the content of the substance under test is determined by the amount of amine formed, such errors are eliminated, as the nitro group is determined in the form of the amino group into which it is converted quantitatively.

The reducing agents used are solutions of salts of variable valency such as vanadium, chromium, titanium, tin and, also, zinc dust.

The first four reagents are used in determinations by the amount of reducing agent used; the use of salts of bivalent vanadium (vanadatometry) gives the most precise results.

Zinc dust in an acidic solution is used in determinations by means of reduction with subsequent diazotization.

232. Reduction with Zinc Dust in Hydrochloric Acid Solution

The reduction of a nitro compound to an amino compound and the quantitative determination of the amine — is the procedure commonly used for the analysis of nitro compounds. It is especially convenient for analyzing nitro compounds that form readily diazotizable amines on being reduced. In this case zinc dust in hydrochloric acid solution is the reducing agent that is usually used.

The analysis is carried out in two stages:

(1) reduction of the nitro compound:

$$RNO_2 \xrightarrow{Zn,\ HCl} RNH_2$$

(2) diazotization of the resulting amino compound:

$$RNH_2 \xrightarrow{NaNO_2,\ HCl} RN_2Cl$$

This method is sufficiently simple and reliable for industrial analyses and does not require special equipment. Reduction takes place quantitatively and any side reactions that are liable to occur do not affect the completeness of conversion of the nitro group to the amino group and, consequently, the test results.

The first stage of the analysis is the reduction of the nitro compound to an amine.

Reduction is carried out in an aqueous or alcoholic solution in the presence of a large quantity of acid. The choice of the solvent depends on the solubility of the given nitro compound. Compounds that are soluble in water (for example, nitrobenzenesulphonic acid) are dissolved in an abundant volume of water; nitrobenzene, nitroanisoles, nitrotoluenes

are dissolved in acetic acid; dinitro derivatives of benzene are dissolved in ethyl alcohol. Hydrochloric acid is added to the solution and zinc dust is introduced into it on heating. Zinc dust is taken in a quantity that considerably exceeds the amount required theoretically. The reaction mixture is heated for some time to attain complete reduction.

The presence of free acid is absolutely necessary for the normal procedure of the reduction process. Congo paper is used to detect free acid. Commercial nitro compounds, as a rule, are of a yellow, yellow-brown, or red colour. In the course of reduction, the colour of the solution of the nitro compound changes until it is decolourized. This can be observed in a test carried out on filter paper, which is made as follows: dip a glass rod into the reaction mass and smear it on a piece of filter paper. In the centre of the mass there will be black particles of zinc and the liquid will run out around it. At the beginning of reduction this liquid will be coloured; decolouration of the liquid indicates the end of reduction.

When reduction is completed, filter the solution containing the amino compound combined with the hydrochloric acid to free it from the zinc dust that has not entered into reaction. Due to its greater density, the zinc dust will be at the bottom of the vessel. Therefore, first decant the liquid, pouring it into a Buchner funnel; wash the residue in the flask by decantation and then transfer it to the funnel and wash it until it is completely clean.

Collect the filtrate and wash waters in one vessel, cool, transfer to a measuring flask, and make up to the mark with distilled water. Take for the titration an exact volume of the resulting solution by means of a pipette, add hydrochloric acid, and titrate with sodium nitrite solution until a drop of the solution under test causes a coloured spot to appear on starch-iodide paper. The conditions under which titration is conducted and the determination of the end-point of titration do not differ in any way from the procedure described in Sec. 224.

One amino group is formed on reducing one nitro group and one molecule of sodium nitrite is used in the titration. Therefore, the gram-equivalent of the nitro compound against sodium nitrite is numerically equal to its molecular weight.

233. Determination of *m*-Nitrobenzenesulphonic Acid in a Paste of the Commercial Product

Since metanitrobenzenesulphonic acid is soluble in water, the solution for the analysis can be prepared simply as follows: dissolve an accurately weighed portion of the paste in distilled water, add hydrochloric acid, and heat to 90°C. At this temperature add zinc dust in small portions and heat the mixture for 10-15 minutes. Metanitrobenzenesulphonic acid is not volatile; reduction can, therefore, be carried out in an open porcelain beaker. After checking for completeness of reduction (colourless liquid on filter paper) decant the solution, wash the residue, combine the filtrate and wash waters, and add hydrochloric acid. Cool the acidified solution to 10-15°C and titrate with sodium nitrite solution, allowing the solution to stand at the end of titration for 2 minutes.

The content of metanitrobenzenesulphonic acid in a commercial paste is calculated from the formula

$$x = \frac{225.17\,(a - a_1)\cdot N \cdot 100}{1000 \cdot g}$$

where x = content of metanitrobenzenesulphonic acid in the paste, per cent;
a = volume of sodium nitrite solution used in the titration, ml;
a_1 = correction for the sensitivity of the starch-iodide paper, ml;
N = concentration of the sodium nitrite solution, g-equiv/lit;
g = weighed portion of the metanitrobenzenesulphonic paste, g;
225.17 = gram-equivalent of metanitrobenzenesulphonic acid.

Example. A portion of the metanitrobenzenesulphonic acid (sodium salt) weighing 4.5034 g was transferred quantitatively to a porcelain beaker, dissolved in 100 ml of distilled water, then 100 ml of 10 per cent hydrochloric acid was added to it, and the solution was heated to 90°C. At this temperature 50 g of zinc dust was added in portions, and the mixture heated for another 15 minutes.

The liquid was decanted, the residue washed by decanting through a Buchner funnel with three 100-ml portions of hot distilled water, and the filtrate and wash waters were combined. Then 60 ml of 10 per cent hydrochloric acid was added, the solution cooled to 10-15°C and titrated with 0.5*N* sodium nitrite solution.

The volume of the sodium nitrite solution used in the titration was 15.35 ml.

The correction for the sensitivity of the starch-iodide paper was found to be 0.15 ml.

The content of metanitrobenzenesulphonic acid in the commercial paste is

$$x = \frac{225.17\,(15.35 - 0.15) \times 0.5 \times 100}{1000 \times 4.5034} = 38.0\%$$

234. Reduction with Sulphate of Bivalent Vanadium

Vanadatometry is the method used for the quantitative analysis of the nitro group by reducing it to the amino group with a solution of a salt of bivalent vanadium taken in excess:

$$RNO_2 + 6VSO_4 + 3H_2SO_4 \rightarrow RNH_2 + 3V_2(SO_4)_3 + 2H_2O$$

Bivalent vanadium is quantitatively oxidized to trivalent vanadium in an acidic solution. The excess of bivalent vanadium remains in the solution and is titrated with ferric-ammonium sulphate solution:

$$VSO_4 + NH_4Fe(SO_4)_2 \rightarrow V_2(SO_4)_3 + 2FeSO_4 + (NH_4)_2SO_4$$

This titration is conducted in the presence of safranine solution used as indicator in the oxidation-reduction reaction. This indicator is colourless in the presence of reducing agents and turns red in the presence of oxidizing agents. As long as there are ions of bivalent vanadium in the solution, the safranine solution is colourless; after all the bivalent vanadium is oxidized to trivalent vanadium (i.e., at the equivalence point), the first drop of excess oxidant (ferric-ammonium sulphate) added to the solution under test turns the latter red due to the change in colour of the safranine solution. The amount of bivalent vanadium

used for the reduction is determined by the amount of ferric-ammonium sulphate used in the titration.

Salts of bivalent vanadium in solution are readily oxidized in the air. Therefore, the vanadium sulphate solution must be isolated from the air. For this reason freshly boiled distilled water (it contains less dissolved oxygen) is used to prepare the solution which is placed in a flask (with a bottom branch tube) filled with carbon dioxide and kept there in an atmosphere of carbon dioxide fed from a Kipp gas generator or a cylinder. The bottom tube is connected with the titration burette so that air does not penetrate into the flask containing the solution or into the burette when the latter is filled during titration. The flask containing the ferric-ammonium sulphate solution is connected to a second burette in the same way. In order to eliminate the effect of air during titration, the titration flask is closed with a rubber stopper in which are tightly fitted the end of the burette, a tube for admitting carbon dioxide, and a short tube with a Bunsen valve. Such stoppers are fitted on the ends of the burettes containing the vanadium sulphate solution and the ferric-ammonium sulphate solution.

Dissolve the compound under analysis in a suitable solvent, transfer to the titration flask, and add a few drops of safranine solution. For different nitro compounds the solvent can be water, acid or alkali solutions, or organic solvents that are miscible with water. Such solvents are acetone, methyl alcohol, glacial acetic acid, and others. Connect the flask to the burette containing the vanadium sulphate solution by means of the stopper fitted on its end, expel the air from the flask with a stream of carbon dioxide, and add vanadium sulphate from the burette. Allow the solution to stand for some time to achieve complete reduction, then quickly connect the flask to the other burette containing the ferric-ammonium sulphate solution and, on passing carbon dioxide through the flask, titrate the excess of vanadium sulphate. Continue titrating until a red or violet colour appears.

Conduct a blank test under the same conditions, taking for the test an equal volume of the solvent instead of a portion of the solution under test. Since vanadium is not

consumed for reducing in the blank test, it remains in the solution and is titrated with ferric-ammonium sulphate solution. Therefore, the amount of ferric-ammonium sulphate used in the titration in the blank test is greater than that used in the analysis. The difference in the volumes of the ferric-ammonium sulphate used for oxidation corresponds to the quantity of bivalent vanadium used for reducing the nitro compound under test.

Six gram-moles of vanadium sulphate are used to reduce one nitro group. Hence, the gram-equivalent of the nitro compound is equal to $^1/_6$ of its molecular weight. Vanadium sulphate and ferric-ammonium sulphate react in equimolecular quantities. Therefore, the gram-equivalent of the nitro compound against ferric-ammonium sulphate is also equal to $^1/_6$ of its molecular weight.

The analysis of azo compounds is conducted in the same way as the analysis of nitro compounds. The azo group is reduced to the amino group, one molecule of the azo compound forming two molecules of the amino compound:

$$RN = NR + 4VSO_4 + 2H_2SO_4 \rightarrow 2RNH_2 + 2V_2(SO_4)_3$$

Thus, in this reaction, a gram-molecule of the azo compound reacts with 4 moles of the vanadium sulphate. The gram-equivalent of the azo compound against bivalent vanadium, and consequently, against ferric-ammonium sulphate, is equal to $^1/_4$ of its molecular weight.

235. Preparation of Standard Vanadium Sulphate Solution

Various compounds of tetravalent and pentavalent vanadium can be used as the original substance for preparing the vanadium (II) sulphate solution. Some of these are vanadium sulphate, $V_2(SO_4)_5$, vanadium pentoxide, V_2O_5, vanadyl chloride, $VOCl_2$.

Dissolve, with heating, a weighed portion of a vanadium compound containing 0.12-0.13 gram-equivalent of vanadium in 25 per cent sulphuric acid solution. Reduce the vanadium to the bivalent state with zinc dust at 80-90°C. The solution of the bivalent vanadium salt will assume an intense pure violet colour which does not change on adding

more zinc dust. Then filter the solution to remove the excess of zinc dust (that has not entered into reaction), add sulphuric acid to the filtrate, and dilute the mixture with freshly boiled distilled water. The water is previously boiled to remove gases from it, in particular, atmospheric oxygen which can oxidize bivalent vanadium. Pour the prepared solution into a dark glass bottle and keep it in an atmosphere of carbon dioxide without access to air.

The vanadium sulphate solution is not standardized. A blank test is conducted simultaneously with the titration of the compound under test.

Example. To prepare an approximately 0.1*N* solution of vanadium sulphate, VSO_4, a 11.78-g weighed portion of vanadium pentoxide, V_2O_5 (containing 0.13 gram-equivalent of vanadium) was introduced into a glass conical flask to which 200 ml of freshly boiled water and 40 ml of concentrated hydrochloric acid were added; the flask was closed with a stopper carrying a long vertical glass tube and the mixture was heated until the vanadium pentoxide was completely dissolved. To the hot solution (80-90°C) was then added 30 g of zinc dust in small portions, the flask was closed with the stopper carrying the glass tube and heated at a temperature of 80-90°C during 30 minutes.

The solution was filtered in a Buchner funnel through filter paper. After that 20 ml of concentrated sulphuric acid was added to the filtered solution which was then diluted with freshly boiled distilled water to a volume of 1 litre, mixed, and poured into a bottle (with a bottom branch tube) filled with carbon dioxide.

236. Preparation of Standard Ferric-Ammonium Sulphate Solution

When preparing this solution it should be kept from coming into contact with the air in the same way as when preparing the vanadium (II) sulphate solution.

Dissolve ferric-ammonium sulphate in freshly boiled distilled water, filter the resulting solution to free it from undissolved particles, add sulphuric acid, and make the solution up to a definite volume with water.

Standardize the solution iodometrically by displacement titration.

To a fixed volume of the solution accurately measured with a pipette add potassium iodide and sulphuric acid, mix and let stand for several minutes in the dark. An oxidation-reduction reaction takes place: iodide ions are oxidized to iodine by ferric ions which are themselves reduced to ferrous ions:

$$Fe^{3+} + I^- \rightarrow Fe^{2+} + I$$

Iodine is liberated in a quantity equivalent to the quantity of reduced iron; it is titrated with a thiosulphate solution in the presence of starch indicator. The concentration of the ferric-ammonium sulphate solution is calculated from the amount of thiosulphate solution used in the titration:

$$N_x = \frac{N \cdot V}{V_x}$$

where N_x = concentration of ferric-ammonium sulphate solution, g-equiv/lit;

V_x = volume of ferric-ammonium sulphate solution taken for titration, ml;

N = concentration of sodium thiosulphate solution, g-equiv/lit;

V = volume of sodium thiosulphate solution used in the titration, ml.

Example. After 50 g of ferric-ammonium sulphate were dissolved in 300 ml of water, the solution was filtered, 30 ml of concentrated sulphuric acid added to it, and the volume made up to 1 litre with water. Exactly 25 ml of the prepared solution were pipetted into a 200-ml conical flask, then 5 g of potassium iodide and 5 ml of 25 per cent sulphuric acid were added, the flask was stoppered, its contents stirred and allowed to stand in the dark for 5 minutes. After that the liberated iodine was titrated with $0.1N$ thiosulphate solution in the presence of 1 ml of 1 per cent starch solution.

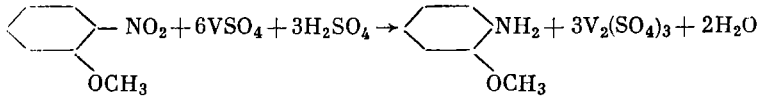
The volume of sodium thiosulphate solution used in the titration was 23.85 ml.

The concentration of the ferric-ammonium sulphate solution was

$$N_x = \frac{23.85 \times 0.1}{25.00} = 0.09540 \text{ g-equiv/lit}$$

237. Determination of *o*-Nitroanisole in the Commercial Product

The content of orthonitroanisole is determined by reducing the nitro group in the compound with vanadium (II) sulphate:



Orthonitroanisole is a liquid that is insoluble in water and in dilute acids and alkalies; it is, however, readily soluble in ethyl alcohol. The alcoholic solution is prepared as follows: dissolve an accurately weighed portion of the orthonitroanisole under test in ethyl alcohol, make up to the mark in a measuring flask with alcohol and, using a pipette, take a portion of the prepared solution for the test. On adding the indicator (1 per cent aqueous solution of safranine) to it, the solution assumes a red colour. After adding an accurately measured volume of the vanadium sulphate solution, the solution under test is decolourized. On titrating the excess of vanadium sulphate with the ferric-ammonium sulphate solution, the first additional drop of the titrant colours the solution red once more.

Simultaneously, conduct a blank test by titrating a volume of ethyl alcohol equal to the volume of the alcoholic solution of orthonitroanisole taken for the titration.

The content of orthonitroanisole in the commercial product is calculated from the formula

$$x = \frac{25.52\,(a-b)\cdot N\cdot V_f\cdot 100}{1000\cdot g\cdot V_p}$$

where x = content of orthonitroanisole, per cent;
a = volume of ferric-ammonium sulphate solution used in titration in the blank test, ml;
b = volume of ferric-ammonium sulphate solution used in the titration of the solution under test, ml;
N = concentration of the ferric-ammonium sulphate solution, g-equiv/lit;
V_f = capacity of the measuring flask, ml;

V_p = capacity of the pipette, ml;
g = weighed portion of orthonitroanisole, g;
25.52 = gram-equivalent of orthonitroanisole.

Example. A portion of commercial orthonitroanisole weighing 0.5104 g was transferred quantitatively to a 100-ml measuring flask, 40 ml of ethyl alcohol were added, and after the substance was dissolved, the solution was made up to the mark with ethyl alcohol.

After that, 10 ml of this solution were pipetted into the titration flask, three drops of safranine solution were added, and the flask connected, by means of a stopper, to the burette containing the vanadium sulphate solution. Carbon dioxide was then passed through it, 40 ml of the vanadium sulphate solution were added, and the flask allowed to stand for 5 minutes, after which the flask was connected to the burette containing the ferric-ammonium sulphate solution (with a concentration of 0.0954 g-equiv/lit) and the excess of vanadium sulphate titrated.

A blank test was carried out simultaneously under the same conditions as follows. To 10 ml of ethyl alcohol in a flask were added 3 drops of safranine solution and 40 ml of vanadium sulphate solution and after 5 minutes, the mixture was titrated with ferric-ammonium sulphate solution.

Suppose that 20.30 ml of ferric-ammonium sulphate solution were used in the titration of the solution under test, and 41.20 ml of ferric-ammonium sulphate solution were used in the titration in the blank test.

The content of orthonitroanisole in the commercial product was

$$x = \frac{25.52\,(41.20 - 20.30) \times 0.0954 \times 100 \times 100}{1000 \times 0.5104 \times 10} = 99.69\%$$

CHAPTER XLVIII

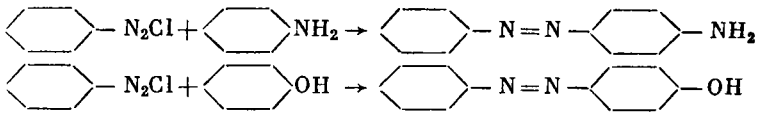
Coupling-Reaction Method

238. General Principles

This method is based on the azo-coupling reaction which is widely used in the manufacture of organic dyes.

When aromatic compounds containing the hydroxyl group or amino group react with diazo compounds, azo

compounds are formed:



Azo compounds are characterized by the presence of the azo group, — N = N —. Hence, the reaction by which these compounds are formed is termed 'the azo-coupling reaction'.

Aromatic compounds with a hydroxyl or amino group in the ring enter into coupling reactions with diazo compounds. Coupling takes place in the para-position with respect to these groups; if the para-position is occupied, coupling occurs in the ortho-position. For analytical purposes, it is essential that the coupling reaction take place quantitatively. This is possible only provided the conditions under which the reaction proceeds are strictly observed: this concerns the temperature, concentration, sequence in which the reagents are added, the pH of the solution, etc.

Not only primary aromatic amines, but also secondary and tertiary aliphatic-aromatic amines (for example, mono- and dimethyl aniline) react with diazo compounds.

The azo-coupling method is used in the analysis of naphthols, naphthol sulphonic acids, amino naphthol sulphonic acids, and certain amines.

When analysis is conducted by means of azo-coupling, a standard solution of a diazo compound (also called the diazo component) is used. The amino or hydroxy compound under test (also called the azo component—not to be confused with azo compound!) is dissolved in a suitable solvent and titrated with the standard solution of the diazo compound from a burette.

As the standard solution is added to the solution under test, the coupling reaction proceeds and, as long as this reaction is not completed, there is an excess of the compound under test in the solution.

At the equivalence point the compound being analyzed is completely converted to the azo compound. The disappearance of the amino or hydroxy compound (determined with the aid of an indicator) marks the end-point of titration. The content of the hydroxy or amino compound is calcula-

ted from the amount of the standard solution of the diazo compound used in the titration.

Depending on the properties of the hydroxy or amino compound under test, appropriate test conditions (i.e., the acidity or alkalinity of the solution, the temperature, the rate at which the diazo compound is added) are chosen.

When analyzing amino compounds, azo-coupling is usually conducted in a slightly acidic solution. To obtain such a solution and maintain a constant hydrogen ion concentration, use is made of a buffer solution, a mixture of acetic acid and sodium acetate.

When analyzing hydroxy compounds, azo-coupling is carried out in a weak-alkaline solution (in a sodium carbonate or sodium bicarbonate solution).

The rate of the azo-coupling reaction depends to a great extent on the acidity or alkalinity of the solution. Departure from specified conditions for conducting this process results in considerable slowing down of the coupling reaction or gives rise to side reactions which lead to erroneous test results.

The temperature at which the coupling reaction is conducted depends mainly on the stability of the diazo compound used for titrating. For instance, titration with diazobenzene is carried out at 0°C, with diazotoluene or nitrodiazobenzene at 15°C. An increase in temperature results in a side reaction (decomposition of the diazo compound) and the test results obtained are too high.

The rate at which the solution of the diazo compound is added depends on the rate at which the coupling reaction proceeds. There should not be any excess diazo compound in the solution under test. If the rate of coupling is high, the titration solution should be added quickly; if coupling proceeds slowly, the titration solution should be added just as slowly: the following portion of the titrant is added only after the preceding portion has reacted fully.

The rate of coupling depends on the structure of the azo component. The presence of electronegative substituents, such as the nitro group, sulpho group, halogens, in the azo component slows down the reaction. Electropositive substituents, such as the hydroxyl group, amino group, methyl group increase the reaction rate. The concentration of hydro-

gen ions in the solution under test also affects the rate of coupling. An optimum pH is specified in each individual case (i.e., for a given pair of interacting azo and diazo components). If the pH is lower than that specified, the rate of diazotization is reduced.

239. Preparation of Standard Solutions of Diazo Compounds

The solutions used for analysis by the azo-coupling method are standardized solutions of diazotized aniline, paratoluidine, paranitroaniline, and certain other aromatic amines. The particular standard solution that is used depends on the character of the compound under test (i.e., of the azo component).

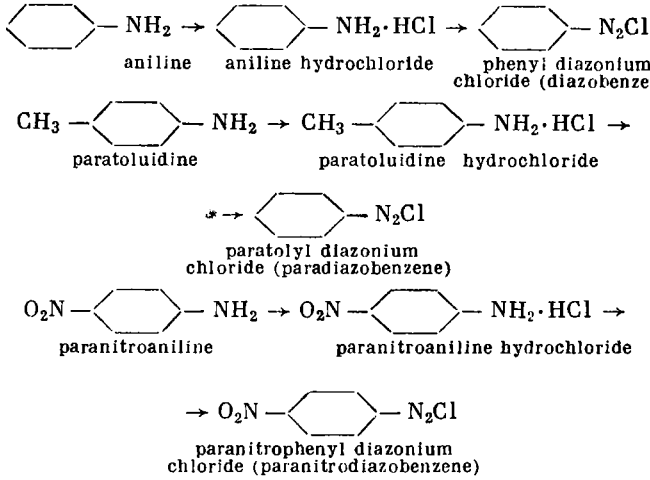
Solutions of diazo compounds are very unstable, therefore, solutions of the hydrochlorides of the respective amines are prepared and standardized against a standard sodium nitrite solution. Such solutions can be kept for a long time. They are subsequently used to prepare solutions of diazo compounds for analysis by the azo-coupling method. The solutions are prepared and standardized as described below.

Dissolve an accurately weighed portion of pure aromatic aniline in distilled water to which hydrochloric acid has been added—at room temperature (aniline and paratoluene) or on heating (paranitroaniline). Transfer the resulting solution of the hydrochloride to a measuring flask, make up to the mark with distilled water, and then standardize the solution against a standard sodium nitrite solution. For this purpose titrate a definite volume of the hydrochloride solution with 0.5 or 1.0*N* sodium nitrite solution under the conditions specified for the given amine: aniline and toluidine are titrated in the presence of potassium bromide at a temperature of 15-20°C and allowed to stand for 10 minutes; paranitroaniline is titrated, without adding potassium bromide, at a temperature of 8-10°C and allowed to stand for 30 seconds.

The solutions of diazo compounds are prepared from the standardized solutions of hydrochlorides of amines directly prior to the analysis in the following way: transfer a definite amount of the solution of the hydrochloride to a mea-

suring flask, add distilled water and, after cooling it in a bath with cracked ice, add an equivalent amount of the standard sodium nitrite solution and two or three more drops of the titrant until a distinct blue spot appears on starch-iodide paper. Then make up to the mark with ice-cold distilled water.

On adding sodium nitrite to the hydrochloride of the respective amine, diazotization takes place and the corresponding diazo compound is formed:


— NH2 → — NH2·HCl → — N2Cl
aniline
aniline hydrochloride
phenyl diazonium chloride (diazobenzene)
CH3 — — NH2 → CH3 — — NH2·HCl →
paratoluidine
paratoluidine hydrochloride
→ — N2Cl
paratolyl diazonium chloride (paradiazobenzene)
O2N — — NH2 → O2N — — NH2·HCl →
paranitroaniline
paranitroaniline hydrochloride
→ O2N — — N2Cl
paranitrophenyl diazonium chloride (paranitrodiazobenzene)

The solution of the hydrochloride should be diluted and diazotized very carefully because the solution is not restandardized; the titre of the prepared solution is calculated from the titre of the original solution of the hydrochloride and, consequently, the actual value will coincide with the calculated value only if dilution is carried out with great precision.

The solutions of diazo compounds are not very stable, as has already been stated. A rise in temperature or sunlight can cause them to decompose. They must, therefore, be kept in a bath filled with ice and in a dark place. But even under these conditions diazobenzene can be kept for not more than 3 hours; diazotoluene, up to 8 hours; paranitrodiazobenzene, for 3-4 hours.

As a result of a rise in temperature, the diazo compound is liable to decompose with evolution of nitrogen:

$$C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

A freshly prepared solution of a diazo compound should be clear. Gas bubbles indicate decomposition of the diazo compound.

240. Titration with Solutions of Diazo Compounds

Because the solutions of diazo compounds used for titrating in the azo-coupling method are unstable, special measures must be taken, when titrating, to obtain exact results.

The solution of the diazo compound is kept in a cold and dark place. Prior to filling the burette, the latter is rinsed with the cold solution and then filled with this solution. Titration is begun at once.

Solutions of particularly unstable diazo compounds (for example, diazobenzene) are cooled during titration. For this purpose the burette is placed in a wide-bore glass cylinder filled with water and ice. A burette cooled in this way is also used when the coupling reaction proceeds slowly and titration takes a long time.

The solution under test is placed in a titration beaker, sodium acetate or sodium carbonate solution is added to it and the solution is then titrated, stirring constantly, with the solution of the diazo compound.

Titration is carried out at the temperature specified for each particular compound. For instance, diazobenzene is always titrated at 0-3°C, diazotoluene at 15°C. Accordingly, the solution under test is cooled by placing the beaker containing it in a bath with a cooling mixture or by introducing crushed ice into the solution itself. The compounds formed by azo-coupling are dyes. Therefore, the solution under test is intensely coloured and the end-point of titration is determined by special procedures.

The end of the coupling reaction is determined by a test which is carried out as follows. Wet the end of a stirring rod with the solution under test and draw a line with it on a piece of ash-free filter paper. The dye will be in the

middle of the streak and the colourless liquid at the fringes. If titration is not completed, the liquid will contain the azo component which is detected with the aid of an indicator solution consisting of a 10-fold diluted solution of the diazo component used for titration. If titration is conducted, for instance, with a 0.1*N* diazobenzene solution, the indicator solution is prepared by diluting 10 ml of this solution with ice-cold water to a volume of 100 ml. A streak of the indicator solution is applied with a clean stirring rod next to the streak of the solution under test. If the latter contains any azo component a coloured streak will appear at the line where the liquids merge.

Titration is usually conducted until a colourless streak is obtained where the liquids that run out of the streaks of the solution under test and indicator solution merge.

Sometimes, however, the solution under test is checked for absence of excess diazo compound (which may appear, for instance, on introducing the standard solution too rapidly in the process of titration). In this case a similar test is also conducted but with another indicator solution (a soda solution of H-acid, 1,8-aminonaphthol-3,6-disulphonic acid). If there is an excess of the diazo compound in the solution, a red streak will appear at the merging line.

The recommended procedure for determining the end-point of titration (by the disappearance of the azo component or by the appearance of excess diazo component) is, as a rule, specified in industrial methods of analysis.

If a soluble dye is formed as a result of the azo-coupling reaction, it is difficult to obtain a colourless streak on filter paper. In this case it is necessary to salt the dye out by adding sodium chloride to the solution under test or directly on the filter paper.

Some practice is needed for proficiency in determining the end-point of titration in analyses by the azo-coupling method.

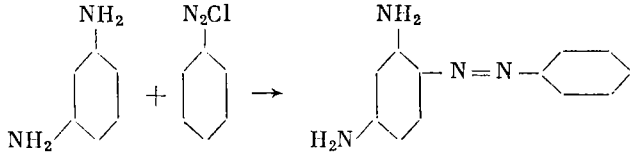
241. Analysis of *m*-Phenylenediamine

Metaphenylenediamine is an active azo component in azo-coupling reactions. It contains in its molecule a second amino group (in the meta-position with respect to the first

amino group) that considerably accelerates the rate of coupling with the diazo compound. In this analysis, dissolve an accurately weighed portion of metaphenylenediamine in warm water, make up to the mark in a measuring flask and, after cooling, transfer a definite portion of the solution by means of a pipette to a titration beaker.

Since metaphenylenediamine, like all amino compounds, is coupled in a slightly acidic solution, prior to titration add acetic acid and sodium acetate to the solution under test. Metaphenylenediamine in such a solution is quantitatively coupled with diazobenzene or diazotoluene. The titration temperature depends on the diazo component chosen. The indicator used in the titration is a solution of the diazo component diluted 10 times. In the course of titration, check for the presence of metaphenylenediamine in the solution under test by coupling streaks of this solution and the diazo-compound indicator solution on filter paper. Continue titrating until the merging streak is colourless.

Equimolecular quantities of the reagents react in this azo-coupling reaction:



The gram-equivalent of metaphenylenediamine in this reaction is numerically equal to its molecular weight. The content of metaphenylenediamine in the commercial product is calculated from the formula

$$x = \frac{108.15 \cdot a \cdot N \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where x = content of metaphenylenediamine in the sample, per cent;

a = volume of the diazo-compound solution used in the titration, ml;

N = concentration of the diazo-compound solution, g-equiv/lit;

V_f = capacity of the measuring flask, ml;
V_p = capacity of the pipette, ml;
g = weighed portion, g;
108.15 = gram-equivalent of metaphenylenediamine.

Example. A portion of commercial metaphenylenediamine weighing 10.8150 g was dissolved in warm distilled water and the resulting solution was transferred to a 1000-ml measuring flask, cooled, and made up to the mark with distilled water. Then 25 ml of the metaphenylenediamine solution was pipetted into a titration beaker, after adding 100 ml of 20 per cent sodium acetate solution and 10 ml of 1*N* acetic acid solution cracked ice was introduced into the solution, and it was titrated at a temperature of 0-3°C with 0.1*N* diazobenzene solution from a burette cooled with the aid of ice. Titration was continued until the diazobenzene indicator solution no longer produced any colouring in the test on filter paper.

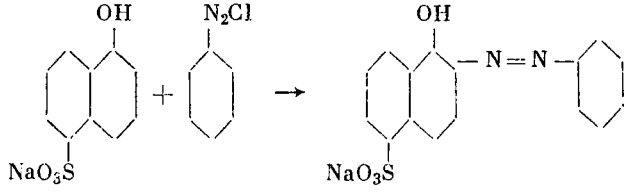
Suppose that 24.42 ml of 0.1*N* diazobenzene solution was used in the titration.

The content of metaphenylenediamine in the product under test was

$$x = \frac{108.15 \times 24.42 \times 0.1 \times 1000 \times 100}{1000 \times 10.8150 \times 25} = 97.68\%$$

242. Determination of Naphthol Sulphonic Acid in the Commercial Product

This acid is commercially produced as 1-naphthol-5-sulphonic acid or its sodium salt. Coupling with diazo compounds, in this case, takes place in the ortho-position with respect to the hydroxyl group:



The sulpho group contained in the molecule of the acid decreases its activity as the azo component in the coupling

reaction which is carried out in a soda solution. As in the previous case, titration is conducted either with a diazobenzene solution or diazotoluene solution and the coupling temperature depends on the diazo component chosen. The indicators used for determining the end-point of titration are diluted solutions of the diazo component. Titration is continued until there is no longer any naphthol sulphonic acid in the solution.

The content of the naphthol sulphonic acid in the commercial product is calculated from the formula

$$x = \frac{246.13 \cdot a \cdot N \cdot V_f \cdot 100}{1000 \cdot g \cdot V_p}$$

where x = content of the naphthol sulphonic acid in the commercial product, per cent;
a = volume of the diazo-compound solution used in the titration, ml;
N = concentration of the diazo-compound solution. g-equiv/lit;
V_f = capacity of the measuring flask, ml;
V_p = capacity of the pipette, ml;
g = weighed portion of the commercial product, g;
246.13 = gram-equivalent of naphthol sulphonic acid.

Example. A portion of commercial naphthol sulphonic acid weighing 24.613 g was dissolved in 300 ml of distilled water, the resulting solution was transferred quantitatively to a 1000-ml measuring flask, and made up to the mark with distilled water. Then 25 ml of the resulting solution was pipetted into a titration flask, 100 ml of 10 per cent sodium carbonate solution and cracked ice were added, and when the solution was cooled to 2-3°C, it was titrated with 0.1*N* diazobenzene solution also cooled to that temperature. Titration was continued until no colouring was observed in the test on filter paper with the diazobenzene indicator solution.

Suppose that 8.24 ml of 0.1*N* diazobenzene solution were used in the titration.

The content of naphthol sulphonic acid in the commercial product was

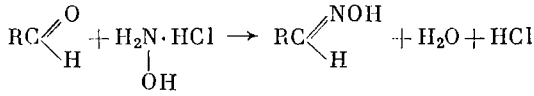
$$x = \frac{246.13 \times 8.24 \times 0.1 \times 1000 \times 100}{1000 \times 24.6130 \times 25} = 32.96\%$$

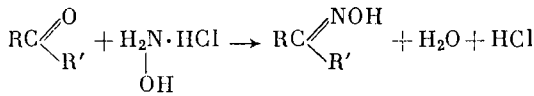
CHAPTER XLIX

Analysis by Oxime-Formation

243. General Principles

This method is based on the action of hydroxylamine hydrochloride on organic compounds containing the carbonyl group:





As a result of this reaction, an oxime (a compound containing the oximino group, =NOH) and hydrochloric acid are formed. One molecule of hydrochloric acid is formed per each carbonyl group. Therefore, the content of the organic compound under test can be calculated from the amount of acid formed.

This method can be used for the analysis of many compounds that contain the carbonyl group; it is most frequently used, however, for the quantitative analysis of aldehydes and ketones.

Two solutions are used in this analysis: an aqueous (or alcoholic) solution of hydroxylamine hydrochloride and a standard alkali solution.

The analysis is conducted as follows: add to a weighed portion or an accurately measured volume of the solution to be analyzed an accurately measured volume of hydroxylamine hydrochloride solution and, after some time has elapsed, titrate the hydrochloride acid produced with sodium hydroxide solution. The indicator used in this titration is methyl orange or bromphenol blue (which changes colour from green-yellow in an acidic solution to blue-green in an alkaline solution).

In oxime-formation one molecule of an aldehyde or ketone reacts with one molecule of hydroxylamine hydrochloride and one molecule of hydrochloric acid is formed. Hence, the

gram-equivalent of the aldehyde or ketone against hydroxylamine hydrochloride and, consequently, against sodium hydroxide is numerically equal to its molecular weight.

Hydroxylamine hydrochloride itself does not react with the sodium hydroxide solution, but its aqueous solution may contain traces of acid. To eliminate erroneous results due to the presence of these traces, a blank test is made simultaneously to determine the amount of alkali used to bind the free acid in the hydroxylamine hydrochloride solution. The correction obtained is subtracted from the volume of the alkali solution used in the titration of the solution under test.

Aldehydes and ketones of low molecular weight, such as formaldehyde, acetaldehyde, acetone and methyl-ethyl ketone are quantitatively converted to oximes at room temperature. Certain aromatic ketones require a high temperature for quantitative formation of oximes.

244. Preparation of Hydroxylamine Hydrochloride Solution

For analysis of aldehydes and ketones of low molecular weight that are soluble in water (formaldehyde, acetone, etc.) the aqueous solution of hydroxylamine hydrochloride is prepared as follows. Dissolve a weighed portion of hydroxylamine hydrochloride in a small quantity of distilled water, transfer to a measuring flask, and make up to the mark with distilled water. To prepare 1 litre of 0.1*N* solution, take 6.95 g of hydroxylamine hydrochloride.

For the analysis of substances that are not soluble in water but are soluble in alcohol, prepare an alcoholic solution of hydroxylamine hydrochloride.

The hydroxylamine hydrochloride solution is not standardized. Compounds containing the carbonyl group are analyzed by adding an excess of the hydroxylamine hydrochloride solution to the solution under test and then titrating the hydrochloric acid, that is formed in a quantity equivalent to the quantity of the substance being tested, with standard sodium hydroxide solution. The content of the substance under test is calculated from the amount of sodium hydroxide solution used in the titration.

245. Determination of Formaldehyde in Commercial Formalin

Formalin is the term for an approximately 40 per cent aqueous solution of formaldehyde. The latter is a gas and to avoid loss on evaporation when determining its content in formalin, it is necessary to cool the solution under test with ice. Proceed as follows.

Place an accurately weighed portion of formalin in a measuring flask and make up to the mark with distilled water. Transfer, with the aid of a pipette, an exact volume of the hydroxylamine hydrochloride solution to the titration flask (a conical flask with a ground-in stopper) and cool it in a bath containing ice. Pipette an accurately measured volume of the diluted formalin solution into the cooled hydroxylamine hydrochloride solution, add a few drops of the indicator solution, mix and, after 5 minutes have elapsed, titrate the hydrochloric acid produced with standard sodium hydroxide solution.

At the same time make a blank test as follows: place in a similar flask a volume of distilled water equal to the volume of formalin taken for titration, add the same volume of hydroxylamine hydrochloride solution and, after allowing to stand, titrate with the sodium hydroxide solution.

The content of formaldehyde in the formalin is calculated from the formula

$$x = \frac{30\,(a-b)\cdot N\cdot V_f\cdot 100}{1000\cdot g\cdot V_p}$$

where x = content of formaldehyde in commercial formalin, per cent;
a = volume of sodium hydroxide solution used in the titration, ml;
b = volume of sodium hydroxide solution used in titration in the blank test, ml;
N = concentration of the sodium hydroxide solution, g-equiv/lit;
V_f = capacity of the measuring flask, ml;
V_p = capacity of the pipette, ml;
g = weighed portion of commercial formalin, g;
30 = gram-equivalent of formaldehyde.

Example. A portion of formalin weighing 1.5000 g was placed in a 250-ml measuring flask and the solution was made up to the mark with distilled water. The titration flask containing 30 ml of 0.1*N* hydroxylamine hydrochloride solution was placed in a bath with ice for 10 minutes and then 25 ml of the diluted formalin solution was pipetted into the flask, its contents stirred, 3 drops of methyl orange indicator added, and the solution titrated with 0.1*N* sodium hydroxide solution.

A blank test was made simultaneously as follows: a mixture containing 25 ml of water and 30 ml of the hydroxylamine hydrochloride solution was titrated with the sodium hydroxide solution until the reaction was neutral to methyl orange.

Suppose that 20.46 ml of sodium hydroxide solution was used in the titration of the solution under test and 0.40 ml of sodium hydroxide solution was used in the titration in the blank test.

The content of formaldehyde in the commercial formalin under test was

$$x = \frac{30\,(20.46 - 0.40) \times 0.1 \times 250 \times 100}{1000 \times 1.5000 \times 25} = 40.12\%$$

PART FOUR
PHYSICOCHEMICAL METHODS OF ANALYSIS

CHAPTER L

Analysis by Physical Measurements

246. Methods of Analysis

Along with the conventional chemical methods of analysis, industrial and research laboratories make extensive use of physicochemical methods, noted for high sensitivity and rapid execution.

In physicochemical analysis the end-point of the analytical reaction (the equivalence point) is determined not visually, but by means of instruments, recording the change in physical properties of the unknown at the equivalence point.

In many cases no chemical reaction is used at all for the analysis, but instead, the values of some physical properties of the substance being analyzed is measured. Such properties may be electrical conductance, light absorption, light refraction, etc.

Three groups of physicochemical methods are of the greatest practical importance for analysis: electrochemical, optical, and chromatographic.

Electrochemical methods are based on the dependence of the electrochemical properties of the substance under test on its composition. These include, in particular, the conductometric, potentiometric, and polarographic methods of analysis.

Optical methods of analysis make use of the relationship between the composition of the unknown and its optical properties. These methods include refractometric, colorimetric, and spectrophotometric measurements.

The chromatographic method is based on the interaction between the substance and a sorbent, and is used for analyzing complex mixtures.

Physicochemical analysis is carried out with the aid of instruments having relatively complex optical or electric systems. That is why these methods are sometimes known as 'instrumental methods of analysis'.

Owing to the simplicity of operation, speed of execution, high accuracy, and high sensitivity physicochemical analysis has found wide application in the chemical, oil refining, petrochemical, metallurgical, and many other branches of industry. These methods are especially valuable because they can be used not only for analyzing products, but in many cases for controlling and regulating industrial technological processes as well.

CHAPTER LI

Conductometric Analysis

247. General

Conductometry is based on measuring the electrical conductance of aqueous solutions of electrolytes.

If certain conditions of measurement are observed, the conductance of an electrolyte solution will depend on its concentration. This forms the basis of the direct method of conductometry, consisting in direct measurement of the conductance of aqueous electrolyte solutions and comparing it with that of solutions of the same composition but known concentration. This method is the most suitable for analyzing solutions containing one definite electrolyte and finds comparatively limited application in laboratory practice. Direct conductometry forms the basis of automatic conductometric control of technological processes and is widely used for automation of production in the chemical and oil refining industries.

Of greater importance for laboratory practice is conductometric titration, a variety of conductometry wherein conductance measurements are used to determine the equivalence point in titration.

248. Principles of Conductometry

Aqueous solutions of electrolytes—acids, salts, and bases—are conductors of electricity. If two platinum plates (electrodes) are immersed in a beaker containing an electrolyte solution and connected with a source of electricity, current will pass through the solution. The intensity of this current is determined by Ohm's law:

$$I = \frac{E}{R} \tag{1}$$

where E = voltage across the electrodes;
R = resistance of the solution.

The ability of a solution to conduct electricity is called conductance.

Conductance is a quantity reciprocal to resistance. If we denote resistance by R, the conductance is

$$L = \frac{1}{R} \tag{2}$$

Resistance is measured in ohms, and conductance in mhos, sometimes written as ohm^{-1}.

The conductance of a solution depends on its concentration, on the properties of the dissolved electrolyte, and on the size and arrangement of the electrodes. The larger the area of the electrodes and the smaller the distance between them, the higher the conductance measured with these electrodes.

To make it possible to compare results of measurements carried out with different electrodes, use is made of the concept of conductivity (specific conductance). Conductivity is the conductance of a solution enclosed between flat electrodes 1 cm^2 in area spaced at a distance of 1 cm from each other.

Conductivity is denoted by the Greek letter $\varkappa$ (kappa) and is measured in $ohm^{-1} \cdot cm^{-1}$.

The conductance of a solution measured by means of any pair of electrodes is given by the formula

$$L = \varkappa \frac{s}{d} \tag{3}$$

where s = area of electrodes, cm^2;
d = distance between electrodes, cm;
$\varkappa$ = conductivity, $ohm^{-1} \cdot cm^{-1}$.

In conductometry the conductance of solutions is usually expressed as conductivity.

Conductivity depends primarily on the concentration and the nature of the electrolyte. The carriers of current in electrolyte solutions are the ions into which the electrolyte molecules break up upon dissociation in aqueous solution. The ions in the solution are in chaotic motion. When a voltage is applied to the electrodes, an electric field arises in the solution, and the ions begin to move in this field, transferring electric charges; in other words, current begins to flow through the solution.

The greater the number of ions participating in transferring the charges, the larger the current and the higher the conductance of the solution. The conductivity of the solutions of most acids, salts, and bases first rises with increasing concentration, but then after a definite maximum is reached, begins to fall off again. This is due to the fact that when the concentration of the solution becomes fairly high, further increase in concentration greatly decreases the degree of dissociation.

The conductivity of a solution also depends on the rate of movement of the current-carrying ions. Different ions move in an electric field at different speeds, and therefore, solutions of different electrolytes of equal concentration have different conductivities. The speed of movement of the ions is characterised by a specific quantity called ionic mobility.

Table 1 lists some ionic mobilities. It is evident from the Table that the hydrogen ion is the most mobile; next comes the hydroxyl ion; the mobilities of all other ions are much smaller. Accordingly, solutions of strong acids and bases have high conductivity.

The numbers in the Table are the distances in centimetres, multiplied by 100,000, traversed by ions in 1 second at a potential gradient of 1 V/cm. To make it possible to compare the mobilities of ions of different charges, they are referred to an ion equivalent. Hence, the notations $^1/_2Ba^{2+}$, $^1/_2SO_4^{2-}$, etc.

Table 1

Mobility of Ions at 18°C

Ion	Ionic mobility	Ion	Ionic mobility
H^+	315	OH^-	171
Na^+	42.8	Cl^-	66.0
K^+	63.9	Br^-	68.0
$^1/_2\,Mg^{2+}$	44.9	I^-	66.5
$^1/_2\,Ca^{2+}$	50.7	$^1/_2\,SO_4^{2-}$	68.4
$^1/_2\,Ba^{2+}$	54.6	NO_3^-	62.3
Ag^+	53.5	$^1/_2\,CO_3^{2-}$	60.5
NH_4^+	63.9	CH_3COO^-	35

Temperature has a noticeable effect on conductance. Raising the temperature by 1°C increases the conductivity by an average of 2 per cent. This is due primarily to the decrease in viscosity of water. The lower the viscosity, the smaller the resistance to movement of the ions, and hence, the higher their speed.

249. Measuring the Conductance of a Solution. Kohlrausch Bridge

Conductances of solutions are measured by means of a Kohlrausch bridge circuit (Fig. 35). If an electric source is connected to A and B, current will flow in each of the bridge arms, its strength depending on the resistance of the arm. The upper arm contains a resistance of known value (reference arm) R and a cell containing the unknown solution (electrolytic cell) R_x. The lower arm is a slide wire with a sliding contact. The diagonal of the bridge is connected to point C in the middle of the upper arm; the other end of the diagonal is connected to the sliding contact S of the slide wire. To measure the resistance R_x, the sliding contact is moved along the slide wire, changing the resistance R until the distribution of currents in the upper and lower arms is such that practically no current flows along the bridge diagonal. A null galvanometer, cut into the diagonal, will show the absence of current. At this moment (it is

called the moment of compensation) the ratio of resistances in the separate parts of the bridge R_a and R_b is as follows:

$$\frac{R_x}{R_a} = \frac{R}{R_b}; \qquad \text{hence,} \qquad R_x = \frac{R_a}{R_b} \cdot R$$

It follows that to calculate the resistance of the solution R_x, it is sufficient to know the ratio of resistances of sections AS and SB, i.e., R_a and R_b.

If the cross section of the slide wire is constant over its entire length, the resistance of any portion of it is proportional to the length of that portion, and the ratio of resistances $R_a : R_b$ in the formula for calculating R_x can be substituted by the ratio of the lengths of the portions $AS : SB$. In the simplest conductometric circuits the slide wire is a smooth straight wire fastened to a wooden rule with divisions (in centimetres) by which the reading is made. In more perfect instruments the ratios R_a: R_b (known as the slide-wire arm ratio) are marked off on the slide wire scale and can be substituted directly into the formula for calculation.

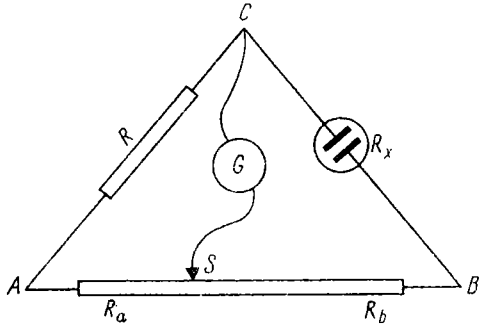


Fig. 35. Kohlrausch bridge

The Kohlrausch bridge operates on alternating current, being plugged directly into the mains. Direct current would cause electrolysis of the solute, since the electrolytic cell would begin to operate as an electrolysis cell.

The vessel for measuring the conductance of a solution, called the electrolytic cell, is a glass vessel with platinum electrodes. The electrodes are fixed in the cell walls or lid

to keep the distance between them unchanged. Depending on the conductance of the solution being analyzed, a cell with electrodes of greater or smaller surface area and with a larger or smaller interelectrode distance is selected. The ratio of electrode area to interelectrode distance is an important characteristic of the cell, known as the electrolytic cell constant.

250. Conductivity Bridge

The design of the conductivity bridge is based on the Kohlrausch circuit. This instrument is a balanced bridge. Its reference arm consists of a resistance box whose resistance R can be varied from 1 to 10,000 ohms. The arm ratio of the measuring resistor can be varied from 0.3 to 3.0 by merely rotating the slide-wire dial, making it possible to measure resistances from 0.3 to 30,000 ohms. The instrument operates on alternating current fed from a 127- or 220-V supply with a frequency of 50 Hz. All the elements of the instrument except the electrolytic cell are mounted on a small panel enclosed in the instrument housing. The top cover of the instrument holds the control dials, instrument scales and terminals for connecting the source of supply and the electrolytic cell.

To measure the resistance of a solution, the instrument is plugged into an alternating current source (with the feed switch in the ∽ position), the solution is poured into a thoroughly washed cell and the cell is connected to the instrument. Before starting measurements, the galvanometer needle is set at its zero position by means of the corrector. Then the resistance of the reference arm is cut into the circuit and the galvanometer needle is returned to zero by rotating the slide-wire dial, first with the galvanometer switch at COARSE, and then at FINE. Take the slide-wire scale reading, write down the resistance of the reference arm and calculate the unknown resistance of the solution from the formula

$$R_x = R \cdot m \tag{4}$$

where R_x = resistance of unknown, ohms;
R = resistance of reference arm, ohms;
m = arm ratio of measuring resistor,

By means of the Kohlrausch bridge, it is not the conductance of the solution that is measured directly, but the reciprocal value, i.e., the resistance. For many analytical problems it is sufficient to determine the resistance of the solution.

The conductance of the solution can be calculated from its resistance by means of formula (2) given in Sec. 248. For example, if the resistance of a solution is 125 ohms, its conductance is

$$L = \frac{1}{R} = \frac{1}{125} = 0.008 \text{ ohm}^{-1}$$

251. Determination of Conductivity of a Solution

The conductivity of an unknown solution is determined by the comparison method of measurement.

For this purpose use is made of a series of electrolytes, the conductance of whose solutions has been measured with great accuracy and from which it is not difficult to prepare solutions of exact concentration. These substances (like primary standards in titrimetric analysis) are used for establishing the conductivity of solutions of other substances. The most commonly used compound for this purpose is potassium chloride. The conductivity of potassium chloride solutions of different concentrations are as follows:

	At 15° C	At 20° C	At 25° C
$1M$	0.09252	0.10207	0.11180
$0.1M$	0.01048	0.01167	0.01288
$0.02M$	0.002243	0.002501	0.002765
$0.01M$	0.001147	0.001278	0.001413

The electrolytic cell is filled with a potassium chloride solution of exact concentration, e.g., $0.1M$, and its conductance is measured at a definite temperature. The results are substituted into formula (3) given in Sec. 248. The conductivity of $0.1M$ potassium chloride solution at the temperature of measurement is known and the s/d ratio is calculated by substituting the known value into the formula. The ratio s/d (the electrolytic cell constant, which is usually denoted by K) characterizes not only the surface area and spacing of the electrodes, but also the size and

shape of the cell, and is a constant for the given electrolytic cell (of course, provided the electrodes are stationary).

Since the value of K remains constant in all measurements made in the given cell, the conductivity of any solution can be calculated by simply measuring its resistance R and substituting it into the formula

$$L = \varkappa \frac{s}{d} = \varkappa \cdot K \tag{5}$$

Hence, the conductivity of the unknown solution is

$$\varkappa = \frac{L}{K} = \frac{1}{K \cdot R} \tag{6}$$

Formula (6) is the basic formula for calculating the conductivity of an unknown solution. As the conductivity of a solution depends on its temperature, measurements must be made at a constant temperature. For especially exact measurements the electrolytic cell is placed in a thermostat where a constant temperature is maintained.

To determine the constant K of an electrolytic cell, rinse the cell with water and then with a potassium chloride solution and fill it up to the mark with the same solution. After the temperature in the cell has become constant, measure the resistance of the solution. Repeat the measurement three times and take the average of three determinations for the calculation. Then empty the cell, wash it with distilled water, rinse it with the unknown solution and fill it up to the mark with the same solution. After the temperature in the cell has become constant, measure the resistance of the solution. Take the average of three determinations for the calculation.

Example. (*a*) *Determination of the electrolytic cell constant.* The concentration of the potassium chloride solution is $0.1M$. The temperature of the experiment is 20°C. The conductivity of a $0.1M$ potassium chloride solution at 20°C, $\varkappa = 0.01167$ ohm^{-1}·cm^{-1}. The resistance of the reference arm $R = 1000$ ohms. The measuring resistor scale readings are: $m_1 = 0.450$; $m_2 = 0.452$; $m_3 = 0.451$; $m_{av} = 0.451$.

The resistance of the potassium chloride solution [by formula (4)] is

$$R_x = R \cdot m_{av} = 1000 \times 0.451 = 451 \text{ ohms}$$

The electrolytic cell constant [by formula (6)] is

$$K = \frac{1}{R_x \varkappa} = \frac{1}{451 \times 0.01167} = 0.19 \text{ ohm}$$

(*b*) *Determination of the conductivity of the solution.* The resistance of the reference arm $R = 100$ ohm. The measuring resistor scale readings are: $m_1 = 0.715$; $m_2 = 0.715$; $m_3 = 0.710$; $m_{av} = 0.713$.

The resistance of the solution under test is

$$R_x = 100 \times 0.713 = 71.3 \text{ ohms}$$

The conductivity of the test solution is

$$\varkappa = \frac{1}{R_x \cdot K} = \frac{1}{71.3 \times 0.19} = 0.738 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$$

252. Determination of the Concentration of a Sodium Chloride Solution from Its Conductivity

The direct conductometric method of determining the concentration of solutions is based on the dependence of the conductivity of the solution on the content of solute in it.

Prepare a series of solutions with known contents of the electrolyte in question and determine their conductivity. Plot the results as conductivity of solution versus concentration. This plot is called a calibration curve. Then determine the conductivity of the unknown solution and using the calibration curve, calculate the content of electrolyte in it.

For example, to determine the concentration of a sodium chloride solution, prepare preliminarily a solution containing 200 g/lit of this substance. Then by diluting this solution, prepare a series of standard solutions containing 40, 60, 80, and 100 g/lit of sodium chloride. Determine the conductivity of these solutions in an electrolytic cell. In the cell, the constant of which was previously determined [see formula (4), Sec. 250], $\varkappa$ equals 0.0510, 0.0730, 0.0940, and 0.1140 $\text{ohm}^{-1} \cdot \text{cm}^{-1}$, respectively. Plot the concentrations on the abscissa against conductivity on the ordinate. Using

this plot or calibration curve, the content of sodium chloride can be determined in a solution containing from 40 to 100 g/lit.

Fill the cell with the unknown solution and determine its conductivity. Suppose it equals 0.1030 $ohm^{-1} \cdot cm^{-1}$. Find the ordinate (Fig. 36) corresponding to this conductivity and draw a horizontal from it to intersect the curve. From the point of intersection drop a perpendicular to the axis of abscissas. The abscissa thus found corresponds to a sodium chloride content of 90 g/lit.

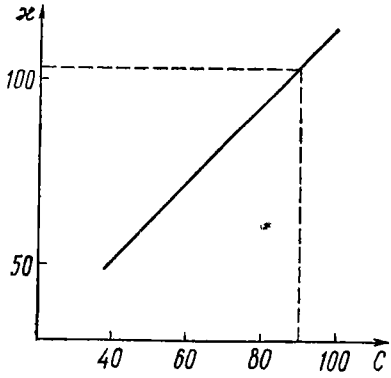


Fig. 36. Concentration versus conductivity curve for sodium chloride solution
C — concentration of sodium chloride; x — conductivity of solution

Most of the time needed for direct conductometric determination of the concentration of a solution is spent on preparing the standard solutions and plotting the calibration curve. The analysis itself takes not more than 10 minutes.

If the same cell is used all the time, the analysis procedure can be simplified. It is not necessary to calculate the cell constant and the conductivity of the solution. The resistance of the standard solutions can be measured and the calibration curve plotted as solution concentration versus solution resistance. Then in analyzing an unknown solution, it is sufficient to measure its resistance and to find its concentration from the calibration curve.

Direct conductometric analysis is very convenient for routine analyses of solutions containing a single electrolyte, especially if the solutions are coloured or turbid. The operation of industrial conductometers (also called concentration meters) is based on the relationship between the concentration of a solution and its resistance. These instruments are widely used for automatic control of solution concentrations at chemical plants.

This method finds but limited application in laboratory practice, because the conductance of a solution depends not only on the concentration of the substance being analyzed, but also on the concentrations of all the ions present in the solution, and therefore the presence of impurities in the unknown solution may give rise to erroneous test results.

253. Conductometric Titration

Conductometric titration is a method of volumetric analysis based on the change in conductance of the solution at the equivalence point.

The original solution contains ions of the substance being analyzed. As the titration progresses the content of ions in the solution changes. The ions of some compounds form slightly dissociated substances, and the ions of others, insoluble compounds. As a result of the chemical reaction, ions of different mobility appear in the solution.

Depending on the nature of the ions, a more or less sharp change in conductance of the solution occurs at the equivalence point. This change depends on how much the mobilities of the ions formed as a result of the reaction differ from the mobilities of the ions removed from the solution by the reaction.

Conductometric titration is used mainly in reactions of neutralization, precipitation, and complex formation. Some of these determinations can be carried out by conventional titrimetric techniques as well, but if the unknown solution is turbid or coloured, conductometric titration makes it possible to determine the end of titration more accurately.

By means of conductometric titration, determinations can be made that cannot be carried out by conventional titrimetric techniques; some examples are analysis of a mixture of sulphuric and hydrochloric acids and mixtures of chlorides and bromides.

In technique of execution, conductometric titration resembles titration in volumetric analysis, differing from it in the method of determining the equivalence point. An exactly measured volume of the unknown is placed in the electrolytic cell and its conductance is measured.

Then the standard solution is added in portions from a burette. After adding each portion, the solution in the cell is mixed and its conductance is determined. Such measurements are carried out until the equivalence point is reached, after which a few more portions of the standard solution are added and the titration is discontinued.

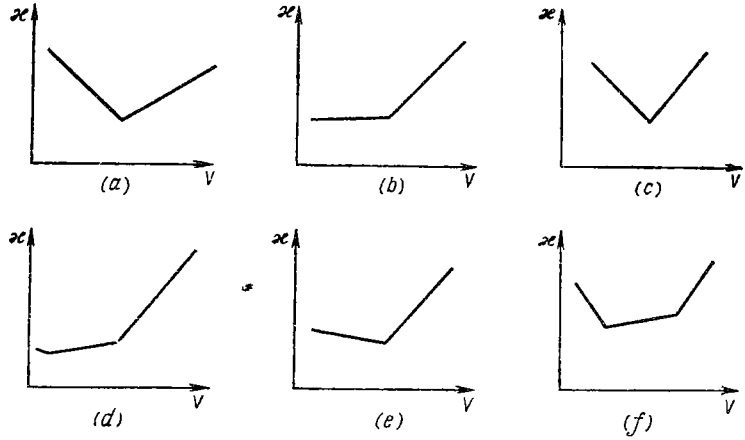


Fig. 37. Conductometric curves for titration of

a — barium chloride solution with sodium sulphate solution; *b* — silver nitrate solution with potassium chloride solution; *c* — hydrochloric acid solution with sodium hydroxide solution; *d* — acetic acid solution with sodium hydroxide solution; *e* — ammonium chloride solution with sodium hydroxide; *f* — mixtures of hydrochloric and acetic acids with sodium hydroxide solution; *V* — volume of standard solution added; *æ* — conductivity

The results of titration are recorded in a table and plotted as a conductometric titration curve, the volume of the standard solution added being marked off on the abscissa and the conductivity on the ordinate.

The resulting conductometric titration curve shows how the conductivity of the solution changed during the titration. At the equivalence point, the nature of the curve changes, a break or inflection appearing. Several types of conductometric titration curves are shown in Fig. 37.

In conductometric titration, a curve with a pronounced break at the equivalence point is rarely obtained. Most often there is an inflection in the curve at this point, and

the equivalence point is found by continuing the rectilinear portions of the curve to their intersection (Fig. 38).

In routine analyses the whole curve is usually not plotted, but only four conductivity values are marked off on the plot: two before the equivalence point and two after it. These points are then connected in pairs and the intersection of the lines connecting each pair corresponds to the equivalence point (Fig. 39).

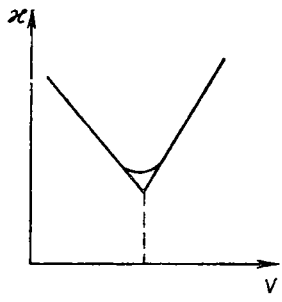


Fig. 38. Determination of equivalence point by rectification of conductometric titration curve
V — volume of standard solution added; $\varkappa$ — conductivity of solution

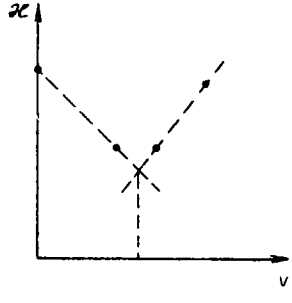


Fig. 39. Determining the equivalence point from four values of conductivity
V — volume of standard solution added; $\varkappa$ — conductivity of solution

The content of the unknown is found from the conventional calculation formula of volumetric analysis:

$$N_x = \frac{V}{V_x} \cdot N$$

where V_x = volume of unknown solution taken for the analysis, ml;
N_x = concentration of unknown solution, g-equiv/lit;
V = volume of standard solution used in the titration up to the equivalence point, ml;
N = concentration of standard solution.

In this case it is not the absolute value of conductivity of the unknown solution that is important, but the nature of its change during the titration. During the titration, the conductivity of the unknown may change due to dilution with the standard solution This does not affect the

result of titration but may make determination of the equivalence point less distinct. To decrease the effect of dilution, standard solutions of maximum concentrations are used.

The nature of the conductometric titration curve may differ depending on the properties of the unknown and the titrant. The following paragraphs deal in greater detail with the most important examples of the use of conductometric titration.

The practical techniques of titration, plotting of the curve, finding the equivalence point, and calculating the results of analysis are identical for most cases and will be discussed on the example of determination of barium chloride by titration with sodium sulphate.

254. Titration of a Solution of Barium Chloride with Sodium Sulphate

The following reaction occurs:

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$$

As the sodium sulphate solution is added to the unknown solution the content of barium ions in the solution decreases. They interact with sulphate ions, precipitating out as barium sulphate. Their place in the solution is taken by an equivalent amount of sodium ions. The mobility of sodium ions is lower than that of barium ions, and hence, the conductivity of the solution decreases. This becomes evident if the conductance of the solution is measured after adding each portion of sodium sulphate solution.

At the equivalence point all the barium ions are converted to barium sulphate, and the conductivity of the solution is at a minimum. Addition of the next portion of sodium sulphate solution increases the concentration of ions in the solution, since the sulphate ions no longer interact with barium ions to form an insoluble compound and remain in the solution. The conductivity of the solution begins to increase. If another portion of sodium sulphate solution is added, the conductivity increases still more. The course if the conductometric titration becomes especially vivid if depicted as a curve (see Fig. 37*a*). The volume of sodium

sulphate solution is marked off along the abscissa in millilitres, and the conductivity of the solution along the ordinate.

The left-hand branch of the curve corresponds to the moment of titration where there are still barium ions in the solution; the inflection point of the curve is the equivalence point, and the section of the curve beyond the equivalence point corresponds to the increase in conductance due to the addition of an excess of sodium sulphate. The conductometric titration curve has such a shape whenever titration involves replacement of ions of higher mobility by ions of lower mobility.

In practice the analysis is performed as follows: place an exactly measured volume of the barium chloride solution under test in the titration cell. This cell may be a beaker with electrodes and an electromagnetic or motor-driven stirrer lowered into it.

It is very important to stir the unknown solution thoroughly during conductometric titration. The electrodes should be completely immersed in the solution. If the measured volume of solution is insufficient for this purpose, distilled water is added to the beaker.

Fill a burette with standard 0.5*N* sodium sulphate solution, measure the conductance of the unknown and start to titrate. Add the sodium sulphate solution in portions of 1 ml, measuring the conductance after the addition of each portion. After the conductivity of the solution begins to increase with further addition (i.e., after the equivalence point is reached) add another three of four portions of the standard solution and then discontinue the titration.

After determining in this way the approximate amount of standard solution needed for titration to the equivalence point, perform a second titration. At first add the titrant in portions of 2 ml, then as the equivalence point is approached, add it in portions of 1 and then of 0.5 ml. As in the first test, after the equivalence point is reached, add another three or four portions of the standard solution.

Record the results in a table and plot a titration curve. The minimum conductivity of the solution corresponds to the equivalence point. From the point of the curve corresponding to the minimum conductivity drop a perpendi-

cular to the abscissa. The point thus found corresponds to the amount of standard solution used in titration to the equivalence point.

To simplify calculations when plotting the conductometric titration curve, the resistance of the solution can be plotted instead of the conductivity. This changes the direction of the titration curve, so that the descending branch becomes the ascending one and vice versa, but the position of the equivalence point and the technique of its determination remain unchanged.

Example. 25 ml of a barium chloride solution were placed in an electrolytic cell and titrated with $0.5N$ sodium sulphate solution. The results of titration were plotted as a curve and the equivalence point was found graphically.

The amount of $0.5N$ sodium sulphate used in the titration was 3.6 ml.

The content of barium chloride in the unknown solution was

$$N_x = \frac{V \cdot N}{V_x} = \frac{3.6 \times 0.5}{25.0} = 0.072 \text{ g-equiv/lit}$$

Results of Titration

V	0	1.0	2.0	2.5	3.0	3.2	3.4	3.5
R	202.8	224.0	245.5	256.3	265.5	267.5	269.5	270.5
V	3.8	4.0	4.2	4.5	5.0	5.5	6.0	
R	270.9	270.0	269.0	265.0	257.5	249.5	242.0	

255. Titration of a Silver Nitrate Solution with Potassium Chloride

The following reaction occurs:

$$AgNO_3 + KCl = AgCl + KNO_3$$

During the titration the silver ions in the solution are substituted by potassium ions. The mobility of potassium

ions is higher than that of silver ions, and therefore on addition of even the first portions of potassium chloride the conductance of the solution increases slightly (slightly because the volume of the solution increases during the titration, which in its turn promotes a decrease of conductance). Hence, the left-hand portion of the curve (see Fig. 37*b*) is a line slightly inclined with respect to the abscissa. At the equivalence point all the silver ions are in the form of silver chloride. The addition of the next portion of potassium chloride solution results in a noticeable increase in conductivity of the solution.

256. Titration of a Strong Acid with an Alkali

The reaction of hydrochloric acid with sodium hydroxide is as follows:

$$HCl + NaOH = NaCl + H_2O$$

In dilute solution a strong acid is completely dissociated, and the conductivity of the solution depends primarily on the content of hydrogen ions. It is evident from Table 1 (see Sec. 248) that hydrogen ions are the most mobile ones. During the titration, the hydrogen ions interact with hydroxyl ions to form water molecules which practically do not dissociate into ions. Instead of the hydrogen ions there appears an equivalent amount of sodium ions in the solution, but the mobility of these ions is several times lower. The conductivity of the solution decreases noticeably. At the equivalence point the acid is neutralized since the hydrogen ions are completely bound by the OH^- ions in water; the only ions in the solution are now sodium and chloride ions, whose mobility is fairly low. At this moment the conductance of the solution is at a minimum. The first portion of alkali added after the equivalence point is reached causes a sharp rise in conductivity, because highly mobile hydroxyl ions appear in the solution (see Fig. 37*c*).

257. Titration of a Weak Acid with an Alkali

Acetic acid is a weak acid with a low degree of dissociation. The amount of hydrogen ions and acid radicals in its solution is insignificant. When acetic acid is titrated with

a sodium hydroxide solution the following reaction ensues:

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

At the start of titration the conductivity of the solution decreases slightly and then begins to rise. This is due to the fact that acetic acid is replaced by sodium acetate, the degree of dissociation of which is about 60 times higher than that of acetic acid. As the titration proceeds the content of ions in the solution increases, and though sodium ions and acetate ions are less mobile than hydrogen ions, the conductivity of the solution, after a slight decline owing to binding of hydrogen ion, increases. Until the equivalence point is reached this increase may be insignificant, but after all the acid is neutralized the addition of the first excess portion of alkali will cause a noticeable rise in conductance (see Fig. 37*d*).

258. Titration of a Salt of a Weak Base and a Strong Acid with a Strong Base

Titration of an ammonium chloride solution with sodium hydroxide results in the formation of a weak electrolyte, ammonium hydroxide:

$$NH_4Cl + NaOH = NaCl + NH_4OH$$

During the titration the conductivity of the solution decreases slightly, because the more mobile ammonium ions are converted to weakly dissociated ammonium hydroxide and an equivalent amount of less mobile sodium ions appears in the solution. At the equivalence point the ammonium ions are completely bound and the conductivity of the solution is at a minimum. The addition of the next portion of sodium hydroxide sharply increases the conductance, because hydroxyl ions appear in the solution (see Fig. 37*e*).

259. Titration of a Salt of a Weak Acid and a Strong Base with a Strong Acid

Titration of a solution of sodium acetate with hydrochloric acid results in the formation of acetic acid, a weak electrolyte:

$$CH_3COONa + HCl = CH_3COOH + NaCl$$

In this case the conductivity of the solution increases slightly during the titration, because the acetate ions are converted to slightly dissociated acetic acid, their place in the solution being taken by the more mobile chloride ions. After the equivalence point is reached, the addition of a new portion of hydrochloric acid sharply increases the conductance owing to the appearance of hydrogen ions in the solution.

260. Titration of a Mixture of Hydrochloric and Acetic Acids with Sodium Hydroxide

Analysis of mixtures of strong and weak acids (or strong and weak bases) is based on the fact that in the presence of a strong acid (base) the weak acid (base) practically does not dissociate. Therefore, at the beginning of titration the standard solution is used up only in neutralizing the strong acid (base) and only after the latter is neutralized, does it begin to neutralize the weak acid (base). This results in two break points on the conductometric titration curve.

Hydrochloric acid is a strong acid and suppresses ionization of acetic acid, whose degree of dissociation is in general very low. During the titration, at first only one reaction occurs:

$$HCl + NaOH = NaCl + H_2O$$

The conductivity of the solution decreases until all the hydrochloric acid is neutralized, i.e., until all the hydrogen ions formed as a result of the dissociation

$$HCl \rightleftarrows H^+ + Cl^-$$

are bound. Further addition of alkali causes neutralization of the acetic acid:

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

Two break points appear on the conductometric titration curve (see Fig. 37*f*), corresponding to two equivalence points: neutralization of hydrochloric acid and neutralization of acetic acid. The amount of acetic acid in the mixture is calculated from the difference of volumes of alkali used in the titration up to the second and up to the first sharp change.

261. High-Frequency Conductometric Titration

In conventional conductometric titration the electrodes are lowered directly into the unknown solution. But the precipitates formed during the titration, resinous substances contained in the solution, etc. contaminate the electrodes, and this may result in error. Besides, if measurements are to be made in aggressive media, special materials resistant to the medium in question have to be selected for the electrodes.

These disadvantages are eliminated in the high-frequency method of conductometric titration. In titration by this method the electrodes are outside the electrolytic cell, e.g., as rings or plates fitting tightly on the outside of the titration beaker. High-frequency current is supplied to the electrodes by a special generator. In the simplest circuit of an instrument for high-frequency titration, the cell with the unknown solution plays the part of a capacitor cut into the measuring circuit. As a result of the change in composition of the solution (i.e., during titration) the conductivity of the solution changes and the capacity of the capacitor, whose plates are the electrodes, and the current flowing through the circuit also change. In conventional conductometric titration the change in current is due only to a change in conductivity of the solution. In high-frequency titration the change in current reflects a change in a number of other physical properties of the unknown solution as well (e.g., dielectric constant). The totality of these changes is manifested in a change in what is known as the quality factor of the circuit, which causes a change in current on the grid of an electron valve cut into the circuit.

If the results of titration are expressed graphically by plotting the volume of standard solution added along the abscissa and the current along the ordinate, the resulting curve, like the curve of a conventional conductometric titration, will have a maximum or a minimum at the point corresponding to the equivalence point.

In high-frequency conductometric titration expensive platinum electrodes can be replaced by electrodes made of other metals, since they are not in contact with the unknown solution.

High-frequency titrimetry is used in reactions of neutralization, precipitation, complex formation, oxidation-reduction, and titration need not necessarily be carried out in aqueous solutions, but also in solutions of organic solvents (nonaqueous titration).

High-frequency titration is used for automatic control and regulation of technological processes at industrial plants.

CHAPTER LII

Potentiometric Analysis

262. General

The potentiometric method of analysis is based on measuring the potential of an electrode lowered into the unknown solution. The magnitude of the potential arising on the electrodes depends on the composition of the solution. This dependence forms the basis of the analytical determinations carried out by the potentiometric method.

The most important of these determinations is measurement of the concentration of hydrogen ions in an unknown solution and potentiometric titration.

In potentiometric titration the equivalence point is determined not visually like in ordinary titration with coloured indicators, but by the sharp change in potential of an electrode immersed in the solution. This eliminates the possibility of errors due to visual estimation of the change in colour of the indicator (especially in turbid or coloured solutions), and makes it possible to carry out titration automatically.

The potentiometric method of determining the concentration of hydrogen ions is widely used in chemical, agrochemical, biological, medical, and other laboratories and is the basic method used in instruments for automatic control and adjustment of technological processes.

263. Potential Arising at the Boundary Between a Metal and a Solution

If a metal plate is immersed in water, some of the metal will pass from the surface of the plate into the solution. This process is caused by the action of water molecules,

which promote the removal of metal ions from the plate surface. The metal ions pass into the solution and the surface of the metal plate becomes negatively charged owing to the electrons remaining on its surface. The ability of ions to pass into solution depends on the nature of the metal, being different for different metals.

If the metal plate is dipped not into water, but into a solution containing a salt of the metal, the passage of ions into the solution will be supplemented by the reverse process, the metal ions passing from the solution onto the plate. An equilibrium is soon set up between these two processes. If a copper plate is immersed in a solution of copper sulphate, the equilibrium attained in this case is written as follows:

$$Cu \rightleftarrows Cu^{2+} + 2e$$

Similarly, in the case of a zinc plate the following equation can be written:

$$Zn \rightleftarrows Zn^{2+} + 2e$$

This is a mobile, dynamic equilibrium. An exchange of ions occurs continuously at the metal-solution interface, the number of ions passing from the metal into the solution per unit time being the same as from the solution into the metal.

If ions have passed from the metal into the solution, an excess of electrons forms on the metal surface, and the metal plate becomes negatively charged. The negative charges on the metal surface attract the positively charged metal ions (cations) that are in the solution. The cations cluster around the surface of the plate, forming a layer of positively-charged particles right at the surface of the metal. Thus, a double electric layer is formed at the boundary between the metal and the solution, which can be compared to an electric capacitor, one plate being the charged metal surface, and the other the layer of ions at the surface. This double layer gives rise to a definite electric charge at the boundary between the metal plate and the solution, known as the electrode potential. The magnitude and sign of this potential depend on the direction and intensity of exchange of ions between the plate (electrode) and the solution. Since the properties of a plate made of a given

metal, e.g., zinc, are in the main constant, the potential depends largely on the properties of the solution, in particular, on the content in it of ions participating in the exchange. Thus, the value of the electrode potential is related to the concentration of the solution in which the electrode is immersed.

The difficulty of determining electrode potential values is due to the impossibility of measuring the absolute potential value of a single electrode.

To carry out the measurement it is necessary to connect this electrode by means of a metallic conductor to a second electrode and to measure the potential difference between them. The second electrode (called a reference electrode) has its own potential. One of the most commonly used reference potentials is the hydrogen electrode. This is a platinum plate saturated with gaseous (molecular) hydrogen under a pressure of 1 atm and immersed in a solution in which the concentration of hydrogen ions is 1 g-ion/lit. The potential of such a hydrogen electrode is conventionally taken as zero. The procedure of conventional selection of zero points is known from the course of physics: for example, the freezing point of water (or melting point of ice) is conventionally accepted as the zero of temperature on the Celsius scale.

Thus, the potential difference between two electrodes, a metal one and a hydrogen one, is conventionally accepted as the potential of the metal electrode. This potential difference is essentially the electromotive force of a galvanic cell formed from two half-elements: a metal electrode immersed in the solution under study and a reference electrode immersed in a standard solution.

In the following, when we speak of an electrode potential we shall mean the potential difference between an indicator electrode and a reference electrode, i.e., the electromotive force (e.m.f.) of an electrode pair.

The electrode potentials which arise when a metal is dipped into a $1N$ solution of its salt at 25°C are called standard potentials. Table 2 lists the standard potentials of some metals.

The second column of Table 2 contains the reactions occurring on the electrodes and giving rise to the potential.

Table 2

No.	Electrode reaction	Standard potential, V
1	$Li - e = Li^+$	−3.045
2	$K - e = K^+$	−2.924
3	$Ca - 2e = Ca^{2+}$	−2.866
4	$Na - e = Na^+$	−2.714
5	$Mg - 2e = Mg^{2+}$	−2.363
6	$Al - 3e = Al^{3+}$	−1.663
7	$Zn - 2e = Zn^{2+}$	−0.763
8	$Fe - 2e = Fe^{2+}$	−0.440
9	$Ni - 2e = Ni^{2+}$	−0.250
10	$Sn - 2e = Sn^{2+}$	−0.136
11	$Pb - 2e = Pb^{2+}$	−0.126
12	$H_2 - 2e = 2H^+$	0
13	$Cu - 2e = Cu^{2+}$	0.337
14	$Ag - e = Ag^+$	0.799
15	$Pt - 2e = Pt^{2+}$	1.188
16	$Au - 3e = Au^{3+}$	1.498

The Table also gives data on the hydrogen electrode, at which the following reaction occurs:

$$H_2 \rightleftarrows 2H^+ + 2e$$

All reactions occurring at electrodes are oxidation-reduction reactions and the readiness with which they proceed depends on the magnitude of the potential. The more negative the potential, the more easily the metal yields electrons and is oxidized.

The magnitude of the potential determines important chemical properties of metals and their ions. For example, metals with lower standard electrode potentials (more electronegative metals) are reducing agents with respect to the ions of metals with higher potentials.

If we arrange the metals in a series with increasing standard electrode potential, they form the electromotive series known from the course of inorganic chemistry. All metals more electronegative than hydrogen reduce hydrogen ions to molecular hydrogen.

If a metal plate is dipped into a solution, the concentration of which is not equal to 1 g-equiv/lit, the potential

that arises will differ from the standard. The dependence of the electrode potential E on concentration is expressed by the Nernst equation:

$$E = E_0 + A \log C$$

where E_0 = standard electrode potential, V;
C = concentration of the solution, g-equiv/lit;
A = coefficient depending on the temperature and on the charge of the ion.

For a single-charged ion at 20°C, $A = 0.058\ V$; at 25°C, $A = 0.059\ V$.

For a double-charged ion at 20°C, $A = 0.029\ V$; at 25°C, $A = 0.0295\ V$.

Thus, two conclusions can be drawn, which are important or practical work.

1. The value of the electrode potential depends on the concentration of potential-determining ions in the solution and on its temperature.

2. To measure the potential, a system of two electrodes are needed: one of which is the indicator electrode, and the other a reference electrode.

However, actual electrode potential values, as a rule, do not coincide with those calculated. This is due to the fact that the potential is affected not only by the ions that directly determine the potential, but also by the other ions present in the solution. That is why it is practically impossible to determine the concentration of a substance in solution directly from the value of the electrode potential.

In potentiometry it is not the absolute values of electrode potentials, that are used, but the change in potential during the analysis, e.g., during titration. This forms the basis of the method of potentiometric titration. Direct readings of electrode potential values are used for determining the concentration of hydrogen ions.

264. Measurement of the Electrode Potential

To measure an electrode potential a system of two electrodes is used. One electrode, the indicator electrode, must be sensitive to the ions present in the solution; the potential arising on it depends on the concentration of these ions.

In analytical practice various kinds of indicator electrodes are used, depending on the composition of the solution to be analyzed. The most commonly used are glass, platinum, and silver indicator electrodes.

The second electrode, the reference electrode, must be insensitive to the ions contained in the solution; its potential is constant and is independent of the composition of the solution.

The hydrogen electrode is inconvenient for carrying out measurements in practice, and for this reason other electrodes ensuring a sufficiently constant and reproducible potential are used as reference electrodes; the most common of these is the calomel electrode. It is a system consisting of metallic mercury, mercurous chloride (calomel), and potassium chloride solution. If a saturated potassium chloride solution is used, the electrode is called a saturated calomel electrode. In the most common design of the calomel electrode, the mercury and a calomel paste are placed in a narrow glass tube closed at the bottom by a porous partition. The tube is sealed into a glass cell which is filled with a saturated solution of potassium chloride.

This electrode is immersed in the solution being analyzed together with the indicator electrode. To make electrical contact between the calomel electrode and the solution being analyzed, the electrode has a loosely fitting ground-glass joint in its lower part and the electrical contact is made through a microcrack in the joint.

The system of two electrodes immersed in the unknown solution constitutes a galvanic cell, the e.m.f. of which is the potential characterizing the composition of the unknown solution.

Measuring the electrode potential or potential difference is not a simple task. The usual instrument used to measure voltage, the voltmeter, is unsuitable for measuring electrode potentials because it uses current during the measurement, which produces considerable errors. Electrode potentials are usually measured by the opposition method of measurement (see circuit in Fig. 40). The e.m.f. of d.c. source *1* is applied across slide wire *2* in opposition to the e.m.f. of electrode circuit *4*. By moving the slider the potential difference impressed on the slide wire is varied until comp-

lete compensation is achieved. At the moment of compensation, i.e., equality of the e.m.f. of the electrodes and the dry cell, galvanometer *3* shows absence of current in the circuit. The e.m.f. of the electrode pair, i.e., the electrode potential is determined by the slider position.

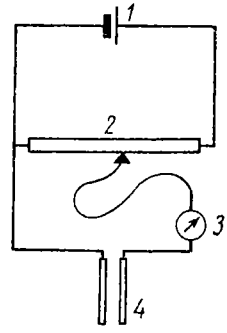


Fig. 40. Potentiometer circuit

1 — d.c. source; *2* — slide wire with sliding contact; *3* — galvanometer; *4* — pair of electrodes

The slide wire may be straight or circular. In modern laboratory pH meters designed for industrial analyses, circular slide wires with sliding contacts are used. Since the cross section of the slide wire is the same over its entire length, its resistivity is also the same over its entire length and the voltage drop on each section is proportional to the length of the section. For example, if a voltage of 1.3 V is supplied from a dry cell to the slide wire, and the latter is divided into 130 sections over its length, the voltage drop across each section is 10 mV. The slide-wire scale, accordingly, also has 130 divisions. If the slider is opposite division 20 at the moment of compensation, the electrode potential equals 200 mV.

When the opposition method of measurement is used, the measuring instruments do not draw any current and this eliminates errors due to the resistance of the system or polarization.

Potentiometric measurements are usually made with laboratory pH meters of several types. The circuit diagrams of these instruments, their operation and field of application are practically identical. Fig. 41 shows a laboratory-type pH meter.

The design of these instruments is based on the above-described measuring circuit. In this circuit the galvanometer serves for establishing the exact moment of compensation, i.e., the moment when there is no current in the circuit. The current arising in the electrode circuit is very weak and has to be amplified with a valve amplifier.

The valve amplifier consists of a bridge circuit containing electron valves (vacuum tubes). It has a galvanometer connected to its diagonal for detecting current zero. After switching on the amplifier and allowing the electron valves to warm up, the amplifier has to be tuned. For this purpose the anode currents of both valves are equalized by means

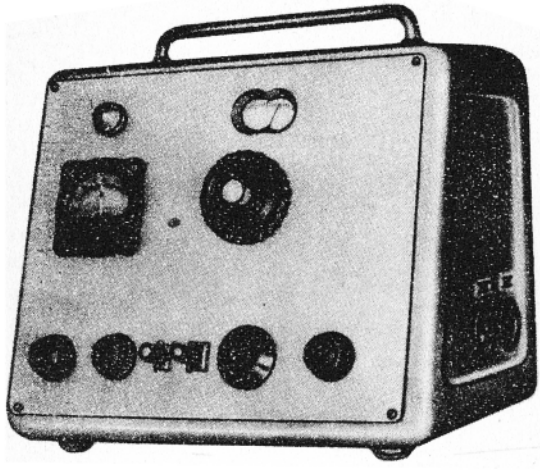


Fig. 41. Laboratory-type pH meter

of a special adjusting resistor. The amplifier is tuned when the pointer of the galvanometer is in zero position.

The potentiometric circuit serves for measuring the e.m.f. of the electrode pair previously amplified by the valve amplifier.

For accurate measurements of the electrode pair e.m.f., the measuring circuit has to be connected to a d.c. source of voltage of specified value remaining constant throughout the measurement. The d.c. source is an important element of the measuring circuit. In laboratory-type pH meters the d.c. source is usually a dry cell or battery. Since the e.m.f. of the latter varies slightly with time, a Weston

cell is usually included in the circuit. It is used as a standard cell owing to the high stability of its e.m.f. (1.0183 V at 20°C). This cell is connected to the circuit to check the e.m.f. of the dry cell. For this purpose the e.m.f. of the standard cell is applied across the slide wire and the e.m.f. of the dry cell is applied in opposition to it; then by means of a special variable resistor the e.m.f. from the dry cell is decreased until compensation occurs, i.e., until there is no current in the circuit. At this moment the e.m.f. delivered from the dry cell is exactly equal to the e.m.f. of the standard cell, i.e., 1.0183 V at 20°C. The operation just described is called tuning the measuring circuit with respect to the standard cell.

When the instrument is ready for the measurement, the e.m.f. of the electrode pair is switched over to the measuring circuit. This upsets the bridge equilibrium and deflects the galvanometer pointer. To compensate this deflection, the e.m.f. of the electrodes is neutralized by the e.m.f. delivered to the slide wire from the dry cell (tuned preliminary with respect to the standard cell). The slide-wire dial is rotated until the galvanometer pointer returns to zero, i.e., until the electrode pair e.m.f. is compensated by the e.m.f. impressed on the slide wire. Then the electrode pair e.m.f. is read off the slide-wire scale.

The potentiometer is used in laboratories to carry out two kinds of analyses:

(1) determination of the concentration of hydrogen ions in a solution;

(2) determination of the concentration of various substances by means of potentiometric titration.

Both determinations are based on measuring the electrode potential which arises when an indicator electrode and a reference electrode are immersed in the unknown solution.

In the former case the analysis consists simply in measuring the potential arising when the electrodes are dipped into the unknown solution. In the latter case the unknown solution is titrated with the electrode pair immersed in it, and the electrode potential is measured after adding each portion of titrant. At the equivalence point a sharp change in the electrode potential occurs after the addition of a single drop of standard solution.

265. Determination of Hydrogen Ion Concentration

Hydrogen ion concentration plays an important part in chemical processes occurring in aqueous solutions.

In neutral solutions the concentration of hydrogen ions equals $[H^+] = 10^{-7}$ g-ion/lit, in acidic solutions $[H^+] > 10^{-7}$ g-ion/lit, and in alkaline solutions $[H^+] < 10^{-7}$ g-ion/lit.

Hydrogen ion concentration is usually expressed by means of its negative logarithm, denoted as pH (from the Latin '*pondus Hydrogenii*' for hydrogen index):

$$pH = -\log [H^+]$$

The hydrogen index is a very convenient means of expressing the nature of a medium:

neutral medium	$pH = 7$
acidic medium	$pH < 7$
alkaline medium	$pH > 7$

The pH of a solution is a very important characteristic. The rate of procedure of a number of chemical reactions and biological processes, the precipitation of substances from solutions, and the composition of the precipitate formed depend on the pH of the medium.

The hydrogen ion concentration has a great effect on the course of biological and chemical processes occurring in the soil, on the delivery of nutritious substances from the soil to plants, etc. The pH-value gives grounds to judge of the properties of soil, of the procedure of soil processes, and to draw conclusions as to the necessity of adding different kinds of fertilizers.

Measurement of pH is widely practised in the chemical, oil processing, pharmaceutical, food, textile, paper, and other branches of industry, as well as in biological, medical, and agrochemical laboratories.

Potentiometric pH determinations are generally made with a glass electrode, which is a thin-walled bulb made of a special grade of glass. When this bulb is immersed in a solution containing hydrogen ions, an exchange of ions occurs between the solution and the bulb surface: the sodium (or

lithium) ions pass from the glass into the solution, and hydrogen ions pass from the solution into the glass. Depending on the hydrogen ion content in the solution, the ion exchange occurs at different rates, and a potential is established at the surface of the glass bulb. The value of this potential depends on the hydrogen ion concentration in the solution, i.e., on its pH-value.

To measure the potential arising on the surface of a glass electrode, a circuit is hooked up containing the glass electrode, a measuring instrument, and a reference electrode. The electrode bulb is sealed to a supporting glass tube. The bulb is filled with a solution of known pH (e.g., 0.1*N* hydrochloric acid solution) and for contact a platinum wire is immersed in it, the end of which is connected via the measuring instrument to the reference electrode.

The thinner the glass used to make the glass bulb, the more accurate and stable the electrode readings. But this makes the bulb very brittle and it has to be handled very carefully; for this reason the bulb is protected by a special cap.

Glass electrodes have a number of advantages over other electrodes. Their potential is established quickly, which is important when measuring pH in a stream of liquid or during potentiometric titration. The potential is practically independent of the presence of oxidizing and reducing agents in the solution; this is very important when measuring pH in industrial solutions. Besides, glass electrodes are cheap and relatively simple to make and handle.

Among the disadvantages of glass electrodes are their brittleness, sensitivity to alkali solutions, and their asymmetry potential.

The properties of the outer and inner surfaces of a glass electrode are not the same, and the potential arising on them may differ from each other. This difference, which is actually a certain additional potential not related to the pH-value of the solution, is called the asymmetry potential and depends primarily on the properties of the glass and the thickness of the glass bulb. The asymmetry potential may somewhat distort the results of measurements. If there were no asymmetry potential, the dependence of the electrode potential on the pH-value of the solution would be constant

and equal to

$$\frac{\Delta E}{\Delta \text{pH}} = 59.1 \text{ mV}$$

i.e., a change in pH of the solution by one unit corresponds to a change in potential of the glass electrode by 59.1 mV.

Actually, owing to the asymmetry potential this dependence is disturbed. To decrease the error due to the asymmetry potential, a new glass electrode should be soaked in water or in 0.1*N* hydrochloric acid solution for 1 or 2 days. As a result, the surface of the glass bulb becomes sensitive to hydrogen ion and simultaneously the asymmetry potential decreases. It does not disappear altogether, but acquires a certain constant value. To eliminate the error of measurement, the readings of the electrode are checked against a buffer solution of known pH-value. This procedure is known as adjustment of the pH scale against buffer solutions.

The distinctive feature of buffer solutions is that their pH-value practically does not change if an acid or an alkali is added to them. Thus, the addition of a buffer solution to any solution maintains a nearly constant pH-value in the latter. This method is often used in analytical practice when some operation (e.g., precipitation) has to be carried out at a definite pH-value.

Table 3 shows the compositions of the most common buffer solutions (known as standard buffers), used for correcting the pH scale.

The pH-value of solutions is measured with the aid of laboratory pH meters. The pH scale of the instrument is preliminarily adjusted against a buffer solution. To do this pour the buffer solution into a beaker and immerse a glass electrode and a calomel electrode into it. If the approximate pH-value of the solution being analyzed is known, select a buffer solution whose pH-value is close to that of the solution being analyzed. Set the temperature compensator knob at the temperature of the buffer solution. Set the switch in the position corresponding to measuring in pH units, tune the amplifier and the potentiometric circuit. Set the slide wire at the pH-value of the buffer solution and connect the electrodes to the measuring circuit

Table 3

Standard Buffer Solutions

No.	Substance	Formula	Concentration of solution	pH	
				at 25°C	at 38°C
1	Hydrochloric acid	HCl	0.1*N*	1.085	1.082
2	Potassium hydrogen bioxalate	$KH_3(C_2O_4)_2 \cdot 2H_2O$	0.1*N*	1.480	1.495
3	Hydrochloric acid Potassium chloride	HCl KCl	0.01*N* 0.09*N*	2.075	2.075
4	Potassium biphthalate	$KHC_8H_4O_4$	0.05*N*	4.005	4.020
5	Acetic acid	CH_3COOH	0.1*N*	4.643	4.640
	Sodium acetate	CH_3COONa	0.1*N*		
6	Monobasic potassium phosphate	KH_2PO_4	0.025*M*	6.855	6.835
	Dibasic sodium phosphate	$Na_2HPO_4 \cdot 2H_2O$	0.025*M*		
7	Borax	$Na_2B_4O_7 \cdot 10H_2O$	0.5*M*	9.180	9.070

by depressing the central button. This will deflect the galvanometer pointer from zero to which it should be returned by turning the asymmetry potential compensator knob. Now the instrument is adjusted against a buffer solution of known pH and measurement of the pH-value of the unknown solution can be started.

Place the solution in a beaker and immerse the electrodes in it (after first rinsing them thoroughly with distilled water), and switching the electrodes into the measuring circuit, rotate the slide wire knob until compensation is attained. Read the pH-value off the slide-wire scale.

Other electrodes used much less frequently for measuring pH of solutions are the antimony and the quinhydrone electrodes.

266. Potentiometric Titration

This type of potentiometric analysis is widely used in laboratory practice. It consists in determining the equivalence point in the titration by a sharp change in the potential difference of a pair of electrodes immersed in the solution under test.

As was shown above, the potential of an indicator electrode depends on the concentration of the ions determining the potential. If the concentration of these ions decreases during titration as a result of the reactions of precipitation, neutralization, or oxidation-reduction, the potential will change correspondingly. The greatest change in potential will occur at the moment when the potential-determining ions are completely bound, i.e., at the equivalence point. Thus, in this case the electrochemical potential is the indicator in the titration.

If the indicator electrode and reference electrode are selected properly, almost all the analyses carried out by titrimetric analyses can be done by the potentiometric method. In addition, the potentiometric method makes it possible to carry out a number of analyses which cannot be done by conventional titrimetric techniques.

Potentiometric titration is generally used for the following reactions of titrimetric analyses: precipitation, oxidation-reduction, and neutralization.

The processes used for potentiometric titration must meet the same requirements as ordinary analytical reactions, *viz*: they must go practically to completion, must proceed at a fast rate and only in a definite direction.

This method of analysis eliminates one of the requirements of classical titrimetric analysis, namely that the end-point of the reaction, i.e., the equivalence point, must be sharply defined visually. This requirement is replaced by another one: at the equivalence point there must be an abrupt change in potential of the indicator electrode.

267. Potentiometric Titration Procedure

Potentiometric titration procedure greatly resembles that of classical titrimetric analysis. The difference is that an electrode pair is immersed in the solution under test and the electrode potential of this pair is measured after adding each portion of titrant. The solution must be stirred thoroughly each time, because the concentration of ions in the liquid layer adjacent to the electrodes and their concentration in the whole solution must be identical. During titration the composition of the solution changes and a new equilibrium electrode potential is set up corresponding to the new composition of the solution. This occurs rapidly, but not instantaneously; therefore, after adding each portion of the standard solution, the titrate must be allowed to stand for a certain time, stirring constantly, after which the electrode potential may be measured.

The results of titration are entered in a table and then plotted as a potentiometric titration curve, marking the volume of standard solution added (in millilitres) on the abscissa and the electrode potential (in millivolts) on the ordinate. At the equivalence point the smooth course of the curve changes. Depending on the magnitude of the abrupt potential change, an inflection (in case of a small change) or a step appears on the curve. The abscissa of the point corresponding to the abrupt change in potential is the volume of standard solution used up to the equivalence point.

The accuracy of this graphical technique is quite sufficient for ordinary industrial analyses. Figure 42 shows curves for different cases of potentiometric titration.

In the case of more complex analyses a differential potentiometric titration curve is plotted, laying off the volume of standard solution (in millilitres) as abscissas and the change in potential corresponding to 1 ml of titrant added as ordinates. At the start of titration the potential changes

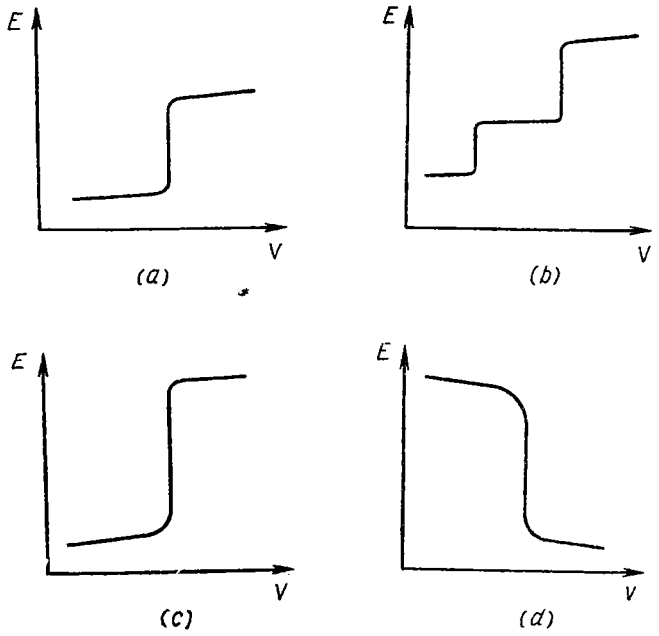


Fig. 42. Potentiometric curves for titration of
a — sodium chloride solution with silver nitrate solution; *b* — mixtures of sodium chloride and sodium iodide with silver nitrate solution; *c* — ferrous salt solution with potassium permanganate solution; *d* — hydrochloric acid solution with sodium hydroxide solution; *V* — volume of standard solution added; *E* — potential

insignificantly even if a large portion of the standard solution is added. As the equivalence point is approached, each portion of standard solution causes a greater and greater change of potential. The maximum (abrupt) change of potential occurs at the equivalence point. If $\Delta E/\Delta V$ (ΔV being the volume of the portion of titrant just added, and

ΔE the change of potential caused by adding this portion of titrant) is plotted on the ordinate, the maximum of this curve will correspond to the equivalence point. A differential potentiometric titration curve is shown in Fig. 43.

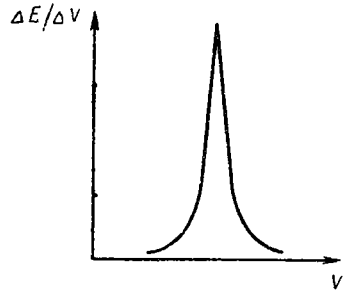


Fig. 43. Differential potentiometric titration curve

V — volume of standard solution added; ΔV — volume of portion of the titrant just added; ΔE — change in potential due to adding this portion

The potentiometric titration curve is necessary for precise determination of the equivalence point, and then of the amount of standard solution used. In many industrial analyses, where the potential changes sharply at the equivalence point, the consumption of standard solution can be determined without plotting a curve. After determining the amount of titrant used, further calculation is carried out by the usual formula of titrimetric analysis:

$$N_x = \frac{V \cdot N}{V_x}$$

where N_x = concentration of unknown solution, g-equiv/lit;
V_x = volume of unknown solution, ml;
N = concentration of standard solution, g-equiv/lit;
V = volume of standard solution used in the titration up to the equivalence point, ml.

In the general case potentiometric titration requires more time than conventional titration with a coloured indicator. That is why the potentiometric method is used only when it is impossible to carry out the analyses by conventional volumetric-analysis procedure.

268. Potentiometric Titration for Precipitation Reactions

By way of an example let us consider the potentiometric titration of chloride ion with silver nitrate. The indicator electrode in this case is a silver electrode, which is a plate

of sheet silver or a platinum plate coated electrolytically with silver. The reference electrode is a saturated calomel electrode.

Before the start of titration, the solution contains chloride ions and other ions whose presence does not give rise to an electrode potential. During the titration molecules of silver chloride are formed:

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

The solubility of silver chloride is very low and it is precipitated out. Only a small amount of silver ions remains in the solution.

The concentration of silver ions in the solution is easy to calculate. Precipitation of silver chloride begins only when the product of the concentrations of silver ions and chloride ions in the solution exceeds the solubility product of silver chloride. During the titration the concentration of chloride ions decreases and the concentration of silver ions increases accordingly. But since the solubility of silver chloride is very low, the concentration of silver ions in the solution even at the equivalence point (i.e., at the moment when all the chloride ions are bound) cannot be higher than 1.3×10^{-5} g-ion/lit (since $[Ag^+] = \sqrt{S_{AgCl}}$).

At the moment when all the chloride ions are bound, the addition of the next portion of silver nitrate solution sharply increases the concentration of silver ions in the solution. Since the electrode potential-determining ions are in this case silver ions, the potential will change sharply at this moment, indicating that the equivalence point has been reached. Plotting the volume of silver nitrate solution added on the abscissa and the potential on the ordinate, we get the potentiometric titration curve (see Fig. 42*a*).

269. Titration of Sodium Chloride with Silver Nitrate

Pipette an exact volume of the unknown sodium chloride solution into a beaker for potentiometric titration provided with a stirrer. Fix the silver electrode in position so that it is immersed in the unknown solution. The reference electrode, a saturated calomel electrode, must not be immersed

directly in the unknown solution, because the potassium chloride solution in the electrode may pass into the titrate and distort the results of the analysis. For this reason the calomel electrode is connected with the unknown solution through a neutral salt bridge, which is a U-tube filled with a solution of ammonium nitrate. A beaker with a saturated solution of potassium chloride is placed next to the titration beaker, the calomel electrode is dipped into the potassium chloride solution and the two beakers are connected through the salt bridge. The tube with the ammonium nitrate is inverted, then one end of it is lowered into the unknown solution, and the other into the potassium chloride solution. Now electrical contact between the calomel electrode and the titrate is made through the ammonium nitrate solution; this prevents chloride ions from passing from the calomel electrode into the unknown.

The titration is carried out by adding the silver nitrate selection in portions from a burette and measuring the potential after adding each portion. The silver chloride precipitate formed may entrain silver ions from the solution which leads to erroneous test results. To prevent this, barium nitrate is added to the titrate and the latter is stirred intensively while titrating. During the titration the potential of the silver electrode gradually increases. The first excess drop of silver nitrate solution causes a sharp rise in the conductance of the solution.

The titration is carried out twice. First the approximate amount of silver nitrate solution used in the titration is determined, adding it in portions of 1 ml. During the second titration the solution is first added in large portions, but as the equivalence point is approached the portions are decreased to 1 and then to 0.1 ml.

Example. 25.0 ml of sodium chloride solution were placed in a titration beaker and titrated with 0.1*N* silver nitrate solution. The titration results are given on p. 476, where

V = volume of standard silver nitrate solution used in the titration, ml;

E = potential, V.

The equivalence point lies between 13 and 14 ml.

The volume of standard silver nitrate solution used in the titration up to the equivalence point is 13.35 ml.

Results of Preliminary Titration

V	0	1	2	3	4	5	6
E	0.237	0.239	0.242	0.243	0.245	0.247	0.249
V	7	8	9	10	11	12	13
E	0.251	0.253	0.255	0.258	0.261	0.265	0.272
V	14	15	16	17			
E	0.305	0.309	0.312	0.315			

Results of Second Titration

V	0	10	11	12	13	13.1	13.2	13.3
E	0.230	0.255	0.258	0.262	0.269	0.271	0.274	0.278
V	13.4	13.5	13.6	13.8	14.0	15.0	16.0	
E	0.293	0.297	0.299	0.302	0.304	0.309	0.312	

The content of sodium chloride in the unknown solution is

$$N_x = \frac{V \cdot N}{V_x} = \frac{13.35 \times 0.1}{25.00} = 0.0534 \text{ g-equiv/lit}$$

270. Titration of a Solution of Sodium Chloride and Sodium Iodide with Silver Nitrate

In potentiometric titration by the precipitation method a sharp change in potential occurs at the equivalence point if a substance of very low solubility is formed during the

titration. In this case the first excess drop of titrant sharply changes the electrode potential. The potentiometric method makes it possible to determine chlorides and iodides quantitatively when they are present simultaneously in the solution.

The solubility of silver iodide (2.8×10^{-6} g/lit) is much lower than that of silver chloride (1.8×10^{-3} g/lit). Therefore, when a solution containing, say, a mixture of sodium chloride and sodium iodide is titrated with a silver nitrate solution, the iodide ions will precipitate first. After all the iodide ions are precipitated, the next drop of silver nitrate solution will cause an abrupt change in potential. Now the chloride ions begin to precipitate, and the electrode potential will be determined by the concentration of silver ions corresponding to the total solubility of silver chloride and silver iodide. A second abrupt change in potential occurs at the moment when all the chloride ions are precipitated. The content of chloride and iodide in the unknown solution is calculated from the amount of titrant used in the titration up to the first and up to the second sharp potential change. The titration curve of such a mixture is shown in Fig. 42*b*.

271. Potentiometric Titration for Oxidation-Reduction Reactions

In the cases considered so far, ions of the metal of which the electrode is made participated in the reaction that gave rise to an electrode potential.

Of major importance in potentiometric analyses are processes in which so-called inert electrodes, such as the platinum electrode, participate. If a platinum electrode is dipped into a solution, containing, say, ions of bi- and trivalent iron in a definite equilibrium:

$$Fe^{2+} \rightleftarrows Fe^{3+} + e$$

a potential will arise at the electrode, the value of which depends on the ratio of concentrations of Fe^{2+} and Fe^{3+} ions. According to Nernst's law the electrode potential can be found from the equation

$$E = 0.77 + 0.058 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

where 0.77 is the normal oxidation-reduction potential of the ferric/ferrous system. Changing the $[Fe^{3+}]/[Fe^{2+}]$ ratio will change the potential. No platinum ions pass into the solution, and the potential that arises is due to electron transfer: the platinum electrode takes on electrons from Fe^{2+} ions and transfers them to Fe^{3+} ions. This phenomenon lies at the basis of the use of the platinum electrode in potentiometric titration of a solution of ferrous sulphate or Mohr's salt with a solution of an oxidizing agent such as potassium permanganate. The reaction takes place in acidic solution (e.g., in the presence of sulphuric acid) according to the following equation:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + \\ + 2MnSO_4 + K_2SO_4 + 8H_2O$$

The ionic equation for the reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftarrows Mn^{2+} + 5Fe^{3+} + 4H_2O$$

As more and more potassium permanganate solution is added to the ferrous sulphate solution the content of Fe^{2+} decreases and that of Fe^{3+} increases, the electrode potential increasing accordingly. At the equivalence point all the iron is practically in the form of Fe^{3+}, and the manganese in the form of Mn^{2+}. The addition of the first drop of excess potassium permanganate solution to the unknown gives rise to a new oxidation-reduction system, MnO_4^-/Mn^{2+}.

This is accompanied by an abrupt change in the electrode potential. The graphical representation of the results of titration is a characteristic potentiometric titration curve (see Fig. 42*c*). The greater the potential difference of the oxidation-reduction processes occurring, the larger the potential change at the equivalence point. When a ferrous sulphate solution is titrated with potassium permanganate solution the potential change is very sharp, because the standard potential of the Fe^{3+}/Fe^{2+} system equals 0.77 V, while that of the MnO_4^-/Mn^{2+} system is 1.52 V. The abrupt change also depends on the initial concentration of the solution. The higher the initial concentration, the larger the change at the equivalence point. Potentiometric titration in oxidation-reduction reactions using a platinum electrode is widely used in industrial and research laboratories.

272. Determination of Ferrous Sulphate in a Solution of Mohr's Salt

Pipette an exactly measured volume of a solution of Mohr's salt into a beaker furnished with a stirrer, add sulphuric acid, stir the solution, and dip a platinum (indicator) electrode and a saturated calomel (reference) electrode into it.

Fill a burette with 0.1*N* potassium permanganate solution and titrate, adding the standard solution in portions of 1 ml. After adding each portion of titrant and stirring the solution, measure the potential of the platinum electrode, which gradually increases during the titration. After determining the approximate volume of standard solution needed for the titration, carry out a second titration to determine the exact volume of potassium permanganate solution needed to reach the equivalence point, and calculate the content of iron.

Example. 25.00 ml of Mohr's salt solution were placed in a titration beaker and titrated with 0.1*N* potassium permanganate solution.

The equivalence point was between 18 and 19 ml. The volume of standard potassium permanganate solution used in the titration up to the equivalence point was found to be 18.45 ml. The titration results are given on p. 480.

The content of Mohr's salt in the unknown solution was

$$N_x = \frac{V \cdot N}{V_x} = \frac{18.45 \times 0.1}{25.00} = 0.0738 \text{ g-equiv/lit}$$

273. Potentiometric Titration for Neutralization Reactions

To determine the moment of neutralization by potentiometric titration, a glass electrode is usually used as the indicator electrode. The potential of this electrode depends on the content of hydrogen ions in the solution. The reference electrode is a saturated calomel electrode.

During titration, e.g., during the addition of an alkali to an acid solution, the concentration of hydrogen ions decreases, and the potential of the glass electrode changes

Results of Preliminary Titration

V	0	1	2	3	4	5	6
E	0.675	0.677	0.679	0.681	0.683	0.685	0.688
V	7	8	9	10	11	12	13
E	0.691	0.694	0.697	0.700	0.703	0.706	0.709
V	14	15	16	17	18	19	20
E	0.712	0.715	0.720	0.730	0.750	1.372	1.395
V	21						
E	1.410						

Results of Second Titration

V	0	10	15	17	18	18.1	18.2
E	0.680	0.698	0.715	0.724	0.740	0.743	0.749
V	18.3	18.4	18.5	18.6	18.7	18.8	19.0
E	0.761	0.812	1.297	1.344	1.355	1.362	1.370
V	20	21					
E	1.390	1.402					

accordingly. The potentiometric titration curve for a neutralization reaction is shown in Fig. 42*d*. The abrupt potential change depends on the concentration of the solution analyzed. The higher the concentration of acid or alkali, the greater the change in potential at the equivalence point. Especially sharp potential changes are observed when titrating solutions of strong acids and bases.

274. Noncompensation Method of Potentiometric Titration

Potentiometric determinations can be considerably simplified. All the analyses described so far were carried out by the opposition method of potentiometric titration involving compensation. In this method the absolute value of the electrode potential is of no significance, only the abrupt change of potential at the equivalence point being important. This abrupt change in potential can be detected in many cases by means of a simpler measuring circuit, known as the noncompensation circuit.

The simplest circuit consists of two antimony electrodes, one of which is immersed in the unknown solution, and the other into a reference solution. If the analysis is carried out by neutralization, the reference solution has a pH = 7, i.e., the pH-value corresponding to the equivalence point. The solutions are connected through a salt bridge, and the electrodes by means of a galvanometer. If the unknown solution is neutral, the potentials arising on both electrodes are the same and no current will flow in the circuit. But if the solution under test is acidic or alkaline (pH $\neq$ 7), current will arise in the electrode circuit and the galvanometer pointer will be deflected. This dependence forms the basis for the determination of the equivalence point of the titration. The indicator electrode is connected, to the galvanometer terminal with the minus sign (—), and the reference electrode, via a high-ohmic resistance and a switch, to the terminal with the plus sign (+). Titrate the unknown solution as usual. At the moment when the equivalence point is reached the current in the circuit will disappear and the galvanometer pointer will rest in its zero position.

In a more complex circuit, an additional d.c. source is included between the indicator electrode and the galvanometer, so that at the start of titration the galvanometer pointer occupies a position convenient for further observation of the course of the titration. Such a circuit with a platinum indicator electrode and a tungsten reference electrode is used, for instance, for potentiometric titration of bivalent iron with potassium dichromate solution. At the equivalence point the galvanometer pointer is sharply deflected when the last drop of titrant is added.

Noncompensation titration with bimetallic electrodes is used for analyzing alloys, for instance, for the quantitative determination of cobalt, vanadium, chromium, nickel, manganese, and other components of alloys. This method is very popular in the metallurgical industry. It is less widespread in the chemical and oil processing industries.

CHAPTER LIII

Polarographic Analysis

275. Principles and Procedures

This method is based on electrolysis of small amounts of the solute and measurement of the resulting polarization of a mercury cathode immersed in the solution under test.

If a direct current is passed through an aqueous solution of an electrolyte, gradually increasing its voltage, electrochemical processes will begin to occur at the electrodes: reduction at the cathode and oxidation at the anode. These processes called, in total, electrolysis give rise to an additional difference in potential between the electrodes, directed in opposition to the voltage applied to them. This phenomenon is called polarization. One of the reasons for polarization is the change in concentration of ions in the layer of solution adjacent to the electrode.

Concentration polarization lies at the basis of the polarographic method of analysis.

Polarography usually uses a dropping mercury cathode, which is a thick-walled capillary tube communicating with a mercury reservoir. The reservoir is arranged at a much higher level than the capillary tube and is connected to it

with rubber tubing. Under the pressure of the mercury column, droplets of mercury drop from the capillary tube at a steady rate. A contact wire is lowered into the mercury reservoir to connect the mercury with one of the terminals of a d.c. source. Thus, the droplet on the tip of the capillary is an electrode and reduction occurs at its surface. Depending on the capillary diameter, the mercury drops at a higher or lower rate. A mercury droplet that has fallen off the capillary is immediately substituted by another droplet of exactly the same size at the capillary tip. Consequently, the surface area of the electrode remains constant, but its surface is continuously renewed. If this were not so, the metal ions reduced at the mercury cathode and then dissolved in the mercury would gradually change the properties of the cathode.

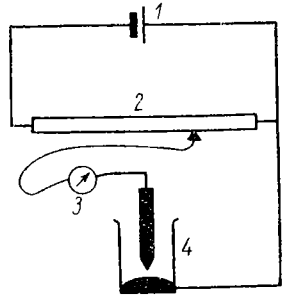


Fig. 44. Polarograph circuit

1 — d.c. source; *2* — slide wire with sliding contact; *3* — galvanometer; *4* — polarograph cell

A polarograph circuit with a dropping mercury electrode is shown in Fig. 44.

Direct current from source *1* flows through slide wire *2* with a sliding contact and galvanometer *3* to the electrodes of polarographic cell *4*. The anode is the mercury placed at the bottom of the cell and connected to the positive terminal of the current source. The cathode is mercury continuously dropping from the capillary tube.

The surface area of the drop hanging on the capillary is very small, whereas the surface area of the mercury anode is fairly large. Accordingly, the current density on the cathode is high, and on the anode, very low[1]. For polarization to occur a definite current density is needed. Therefore, practically no polarization will occur on the large anode area. Hence, only the cathode will be polarized and the voltage applied to the electrodes is spent practically

[1] Current density is the current per unit area of the electrode surface.

only on polarization of the cathode. The voltage drop due to passage of the current through the solution is so insignificant that it can be neglected.

The unknown electrolyte solution is placed in the polarograph cell and the sliding contact is moved to gradually increase the voltage applied to the electrodes. Simultaneously the value of the current passing through the solution is recorded. At first the current in the circuit increases insignificantly. During this period the voltage applied to the electrodes is insufficient for electrolysis. This period corresponds to section *OA* of the polarogram shown in Fig. 45. When the voltage applied reaches a value sufficient for electrolysis of the unknown to begin, further increase of the voltage will cause an immediate increase in current (section *AB* of the curve). At this period the ions in the near-electrode layer are intensively reduced on the cathode surface. Their concentration in the near-electrode layer decreases rapidly. In the rest of the solution the concentration of the ions remains practically unchanged and, as a result of diffusion, they begin to move into the near-electrode layer. Their diffusion, however, is usually much slower than reduction at the cathode; upon further increase of the voltage the rate of diffusion of the ions into the near-electrode layer and the rate of their reduction at the cathode become equal. The current reaches its limiting value (limiting, or diffusion, current). Further increase of the voltage no longer increases the current (section *BC* of the curve).

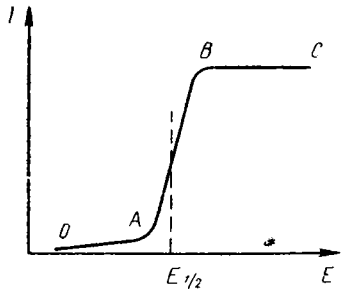


Fig. 45. Polarogram
E — voltage; I — current; $E_{1/2}$ — half-wave potential

The higher the concentration of ions in the solution, the greater the rate of diffusion into the near-electrode layer, and hence, the higher the diffusion current.

The dependence of the diffusion current on the concentration of a given ion in solution forms the basis of the quantitative methods of polarographic analysis.

The polarographic curve shown in Fig. 45 characterizes the unknown solution both qualitatively and quantitatively.

The height of the step, or wave, as it is called, on the curve corresponds to the diffusion current and makes it possible to determine the content of the analyzed substance in the solution.

For qualitative determinations it is important to know the half-wave potential, i.e., the potential corresponding to the middle of the wave. Each ion has its own characteristic half-wave potential, which is independent of the concentration of the ion in the solution. The half-wave potential $E_{1/2}$, measured under specified conditions, is a qualitative characteristic of the ion. The half-wave potentials of some inorganic ions are listed in Table 4.

*Table 4**

Half-Wave Potentials of Metal Ions

Metal	Ion	Supporting electrolyte	Potential of half-wave, V
Bismuth	Bi^{3+}	1*N* HNO_3	−0.10
Iron	Fe^{2+}	0.1*N* KCl or $BaCl_2$	−1.3
	Fe^{3+}	0.5*M* sodium citrate	−0.35
Cadmium	Cd^{2+}	1*N* KNO_3, HNO_3, or H_2SO_4	−0.586
	Cd^{2+}	1*N* KCl or HCl	−0.642
Potassium	K^+	0.1*N* tetramethylammonium chloride	−2.13
Cobalt	Co^{2+}	0.1*N* KCl or NaCl	−1.20
Lithium	Li^+	0.1*N* tetramethylammonium chloride	−2.27
Manganese	Mn^{2+}	1*M* $NH_4OH + 1M$ NH_4Cl	−1.45
	Mn^{2+}	0.2*N* KCNS	−1.55
Copper	Cu^{2+}	0.1*N* KNO_3 or NH_4OCO_4	+0.02
Sodium	Na^+	0.1*M* tetramethylammonium chloride	−2.11
Nickel	Ni^{2+}	1*N* KCl	−1.1
Lead	Pb^{2+}	1*N* KNO_3 or HNO_3	−0.405
Chromium	Cr^{3+}	0.1*M* pyridine + 0.1*N* pyridine hydrochloride	−0.95
Zinc	Zn^{2+}	1*N* KNO_3	−1.012
	Zn^{2+}	2*M* $NH_4OH + 2M$ NH_4Cl	−1.43

* "Chemist's Handbook", Vol. III, Goskhimizdat, Moscow, 1952, pp. 565-575.

Polarography enables analysis of a solution containing a mixture of ions to be made without preliminarily separating them. Since each ion is reduced at a definite voltage, all these ions can be reduced by gradually raising the voltage applied to the electrodes, resulting in the appearance of several steps (or waves) on the polarographic curve. Since definite polarographic wave potentials correspond to definite ions, the particular ions contained in the solution can be determined by measuring the half-wave potentials and referring to suitable tables.

Various methods are used for quantitative polarographic analysis.

The calibration curve method, especially convenient for carrying out routine analyses, consists in preliminarily plotting the polarograms of a number of exact solutions of different concentration. The diffusion (or limiting) current value depends on the concentration of the solution. On the polarograms this dependence is expressed as different wave heights. The wave height is plotted against concentration to obtain the calibration curve, and then the concentration of the unknown solution is determined from this curve by the height of its wave.

The standard solution method consists in plotting the polarogram of a standard solution close in concentration to that of the unknown solution (after plotting the polarogram of the latter) and then calculating the concentration of the unknown from the ratio of the wave heights:

$$C_x = \frac{h_x}{h_0} \cdot C_0$$

where C_x = concentration of unknown;
C_0 = concentration of standard solution;
h_x = height of wave on polarogram of unknown solution;
h_0 = height of wave on polarogram of standard solution.

The accuracy of the determination is sufficient if the concentration of the standard solution is close to that of the unknown solution.

A convenient method for analysis of industrial solutions containing unknown impurities together with the ions to be

determined is the *method of addition*. In this method the polarogram of the unknown solution is first plotted, and then an exact amount of the substance being determined is added and another polarogram is plotted. The content of the substance being analyzed in the unknown solution is calculated from the increase in wave height as the result of the addition.

CHAPTER LIV

Refractometric Analysis

This method is based on determining the refractive index of the unknown substance. The refractive index is one of the main physical properties of a substance; each individual substance is characterised by a definite refractive index.

Of greatest practical importance in the chemical industry is the determination of the index of refraction of liquids, both liquid substances and solutions.

276. Index of Refraction

When a light ray passes from one transparent medium to another, its direction is changed at the interface between the media; the ray is said to be refracted.

The ratio of the sine of the angle of incidence of the ray ($\sin \alpha$) to the sine of its angle of refraction ($\sin \beta$) is called the index of refraction or refractive index n:

$$\frac{\sin \alpha}{\sin \beta} = n$$

If the ray passes into the medium from air, n is the refractive index of the medium with respect to air. For each chemical substance this index depends on its nature and is a constant value (at standard conditions of measurement).

The refractive index depends on the wavelength of the incident light. This accounts for the dispersion of white light on passing through a prism: the individual light rays contained in white light are refracted differently. As a rule, the index of refraction decreases with increasing wavelength (Table 5).

Table 5

Wavelength, mμ	Colour	Symbol	Refractive index of water at 20°C
486	Blue	F	1.3371
589	Yellow	D	1.3330
656	Red	C	1.3311

To obtain reproducible results it is necessary to use for the measurements a light source which gives radiations of a definite wavelength (sodium, mercury, or hydrogen lamps). The refractive index is then designated by a symbol with a subscript indicating the wavelength of the incident light used during the measurement: n_F, n_D, or n_C.

Usually measurements are made at a wavelength of 589 mμ. The source of radiation is a sodium lamp. This lamp requires a special device for switching it on. Besides, work with a lamp giving a radiation of a definite wavelength (monochromatic light) requires a dark room. All this complicates the work.

For industrial analyses measurements are made with an incandescent lamp or in daylight. The instrument is furnished with a special device to compensate the dispersion of white light by the prism and to direct the light beam in the direction coinciding with that of the yellow ray. The refractive index measured in this way practically coincides in value with that measured in monochromatic yellow light. An index of refraction measured by this method is also designated by n_D.

The index of refraction depends on the temperature. With increasing temperature the refractive indices of liquids decrease (see Table 6). Hence, measurements must be made at a constant temperature.

Since the refractive indices of any substance measured at different temperatures are different, the symbol for the refractive index includes, besides the subscript showing the wavelength of the incident light, a superscript to indicate the temperature at which the measurement is made, e.g.: n_D^{20} means that the refractive index was measured at 20°C

Table 6

Substance	Refractive index at a temperature of		
	15°C	20°C	25°C
Aniline	1.5887	1.5861	1.5835
Benzene	1.5043	1.5012	1.4980
Water	1.3334	1.3330	1.3325
Ethyl alcohol	1.3633	1.3613	1.3597

and an incident wavelength of 589 mμ. Handbooks give the refractive indices measured under these conditions (n_D^{20}).

Thus, the most important conditions for obtaining accurate results in refractometric measurements are carrying out the measurements at a definite temperature and a definite wavelength.

However, direct measurement of the values (or ratios) of angles of incidence or refraction at an air-liquid interface is inconvenient. In instruments for refractometric analysis, the angles of incidence and refraction are measured at a liquid-glass interface, using the method described below.

277. Measurement of the Refractive Index by Means of the Angle of Total Internal Reflection

If a light ray passes from a medium of refractive index n_2 into a medium of refractive index n_1, the following relation exists between the angles of incidence and refraction:

$$n_2 \cdot \sin \alpha = n_1 \cdot \sin \beta$$

If the light ray passes from a more refractive medium (with respect to air) into a less refractive one, the angle of incidence α is always smaller than the angle of refraction β.

With increasing angle of incidence the angle of refraction also increases; finally there comes a moment when the angle of refraction becomes 90°, i.e., the ray does not pass into the second medium, but slides along the interfacial boundary (see Fig. 46). This phenomenon is called total reflection and the angle of incidence at which it occurs is called the angle of total reflection φ. Then the equation

becomes

$$n_2 \cdot \sin \varphi = n_1 \cdot \sin 90^\circ; \qquad n_1 = n_2 \cdot \sin \varphi$$

If the ray travels in the reverse direction, namely, from the less refractive to the more refractive medium, a ray incident on the interface at 90° (or close to this value)

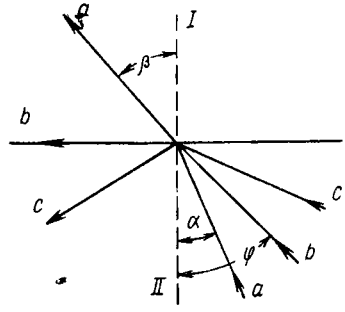


Fig. 46. Total reflection of light

a — ray incident at angle α is refracted at an angle and passes into medium *I*; *b* — ray incident at the angle of total reflection, refracted at 90°; *c* — ray incident at an angle greater than the angle of total reflection; does not pass into medium *I*

will enter the second medium at the angle of total reflection. The grazing ray is refracted at an angle equal to that of total reflection:

$$n_1 \cdot \sin 90^\circ = n_2 \cdot \sin \varphi; \qquad n_1 = n_2 \cdot \sin \varphi$$

If the refractive index of one of the media is known (n_2), it is sufficient to measure the value of the angle of total reflection φ to determine the refractive index of the other medium (n_1).

This principle lies at the basis of the design of instruments for measuring refractive indices, called refractometers. In them, prisms of special grades of glass with high refractive indices are used as the medium of known refractive index. Different types of refractometers based on measuring the angle of total reflection are available. One of the most common types for industrial measurements is the Abbe refractometer.

278. Abbe Refractometer

In this refractometer the light beam passes through a prism consisting of two halves hinged together, between which a drop of the unknown is compressed, forming a layer 0.1 to 0.2 mm thick between them. The light beam passes through one half-prism, called the illuminating prism, then goes through the unknown and passes out through the other half-prism, known as the measuring prism.

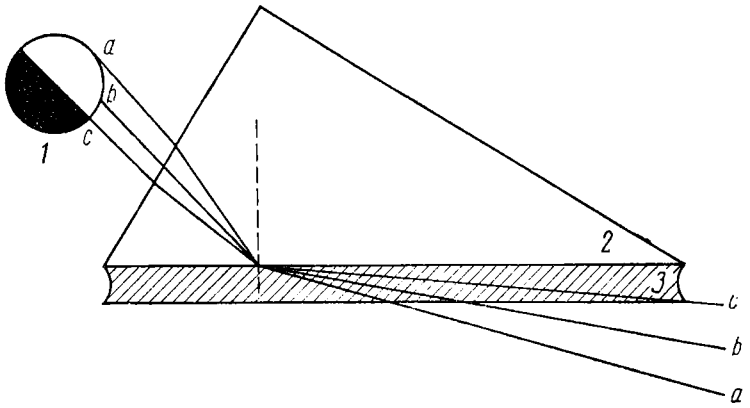


Fig. 47. Refraction of rays on the surface of the measuring half-prism of Abbe refractometer

1 — field of view of eyepiece; *2* — layer of test liquid; *3* — measuring half-prism, *a*, *b*, *c* — refracted rays

Figure 47 is a large-scale drawing of the measuring prism and the layer of the liquid under test. The rays from the light source pass into the illuminating half-prism, are refracted in it, then fall on the layer of test liquid and pass through it onto the surface of the measuring half-prism.

The light beams fall on the surface of the measuring half-prism at various angles. If their angle of incidence is less than 90°, the rays are partly refracted and partly reflected. The refracted rays (*a*, *b*) pass through the measuring half-prism into the observation tube (the greater the angle of incidence, the more the ray is refracted). A ray incident atan angle equal or close to 90° (*c*) is refracted at the angle

of total reflection and also passes into the observation tube. Observing the exit face of the prism through the eyepiece, it can be seen that its right-hand part is illuminated, while its left-hand part is dark. The boundary between the light and dark parts corresponds to the extreme light ray *c*.

The prism is rotated until a distinct boundary between the light and dark fields appears in the eyepiece, dividing the field of view in half. Then the value of the refractive index is read off the instrument scale (which is connected to the prism by means of a special device).

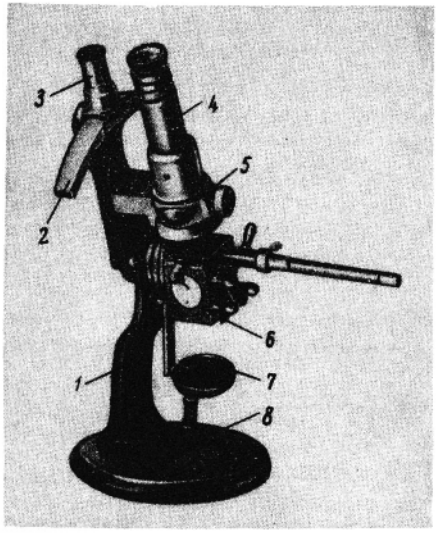


Fig. 48. Refractometer of the Abbe type

1 — stand; *2* — sector-type reading scale; *3* — reading lens; *4* — observation tube; *5* — dispersion compensator; *6* — prism assembly; *7* — mirror; *8* — base

Soviet industry puts out several models of refractometers of the Abbe type, all of which have found application in laboratory practice. They differ in arrangement of the half-prisms, design of reading scale, and range of measurement, but are all identical in principle and method of operation and precision.

One of the most popular laboratory Abbe-type refractometers, designed for measuring refractive indices ranging from 1.3 to 1.7, is shown in Fig. 48.

The main parts of the instrument are the prism chamber (or prism assembly) *6*, sector-type reading scale *2* with reading lens *3*, and tube *4* with dispersion compensator *5*.

The prism assembly consists of two half-prisms (illuminating and measuring), hinged together. The half-prisms are made of heavy flint glass with a refractive index of

$n_D^{20} = 1.740$ and are mounted in metallic double-walled jackets with connecting tubes for circulating water. These jackets have windows cut in them, the light passing in through the bottom window opposite the illuminating half-prism and out through the other window opposite the measuring prism, into the observation tube.

Fixed to an arm underneath the prism assembly is a mirror by means of which the light is directed on the illuminating half-prism. The prism assembly is fixed rigidly by means of a lever to the reading lens of the sector scale. By means of a knob the prism assembly can be rotated about a horizontal axis, while the reading lens moves along the scale. The scale is calibrated in refractive index units.

Above the prism assembly is observation tube *4* mounted over compensator *5* (with its knob on the outside). On the side of the tube is the head of an adjustment screw for setting the zero point of the refractometer when preparing it for work.

All the parts of the instrument are mounted on a frame consisting of base *8* and stand *1*. The tube is fixed rigidly with respect to the prism assembly, but can be rotated together with it and the entire upper part of the instrument about a horizontal axis when placing the substance to be analyzed in the prism chamber.

The optical glass of which the prism is made is very soft and easily scratched. Special care should be exercised when handling the polished working surface of the measuring half-prism. The prism should be wiped with napkins of soft fiber-free cloth.

The unknown is applied to the prism surface with a glass rod or a pipette. The end of the rod should be fused. When applying the unknown, take care that the tip of the rod or pipette does not touch the prism surface.

The zero point of the scale is checked by means of adjusting liquids, i.e., liquids with known refractive indices. In industrial analyses this is most frequently done with distilled water ($n_D^{15} = 1.3334$; $n_D^{20} = 1.3330$; $n_D^{25} = 1.3325$). The zero point should be checked before each series of measurements, but not less than twice each workday.

279. Determination of the Refractive Index of Liquids

Before starting work, wash the working surfaces of the refractometer prism with alcohol and distilled water and then check the scale setting with an adjusting liquid. This liquid is usually distilled water ($n_D^{20} = 1.3330$).

Then wipe the working surfaces of the prism dry and place two or three drops of the unknown between the prisms. Rotate the mirror until the light beam falls on the window of the illuminating chamber and a light field appears in the eyepiece.

Rotate the prism chamber until the boundary between the light and dark fields comes into the field of view and then rotate the compensator knob until a distinct uncoloured boundary is obatined.

Rotating the prism assembly, carefully bring the boundary between the light and dark fields to the centre of the eyepiece crosshairs and read the refractive index off the scale through the reading lens.

Then displace the boundary between the light and dark fields, realign it with the centre of the eyepiece crosshairs and take a second reading. Take five readings in this way and then wash and wipe the working surfaces of the prism, introduce another two or three drops of the unknown, carry out a second series of measurements, and calculate the average refractive index.

During the measurements keep the temperature of the prism chamber constant by passing water from a thermostat through the prism jackets.

Handbook tables usually give refractive indices measured at 20°C. If measurements in the laboratory are carried out at this temperature, the results obtained can be compared directly with tabulated data.

If measurements are made at a temperature other than 20°C, a correction can be made for temperature. For most organic liquids within a temperature interval of 15-25°C, increasing the temperature by 1°C decreases the refractive index by about 0.0005. Hence, if the refractive index of a substance determined at 16°C was $n_D^{16} = 1.3633$, then for

this substance $n_D^{20} = n_D^{16} - (20 - 16) \times 0.0005 = 1.3633 - 4 \times 0.0005 = 1.3613$.

Refractometry is widely used for qualitative and quantitative analysis of individual substances and their mixtures in many branches of the chemical, petrochemical, oil refining, pharmaceutical and food industries.

The refractive index of a substance is an important physical constant that characterizes an individual substance. Commercial products always contain impurities whose refractive indices differ from those of the respective pure products. Hence, the measurement of the refractive index of a commercial product is a useful test for the purity of many products and this index is included in State Standards and Technical Specifications.

For instance, dioctylphthalate used in the plastics industry should have a refractive index within the limits of 1.4830 and 1.4880. The various grades of purified turpentine differ in their refractive index:

	Grade I	Grade II	Grade III
n_D^{20}	1.469-1.472	1.472-1.476	1.476-1.480

Sometimes a particular substance can be identified among a number of substances if their refractive indices are known and differ from each other sufficiently. A more complex characteristic, molecular refraction, is used for the exact identification of substances.

Refractometry is used for the analysis of two-component mixtures, for example to determine the concentration of a substance dissolved in water or an organic solvent. In this case the analysis is based on the dependence of the refractive index upon the content of the solute. Tables are available for some solutions, which give the dependence of the refractive indices on their concentration.

In some cases, the analysis is conducted with the aid of a calibration curve as follows: prepare a series of solutions of known concentration, measure their refractive indices, and plot the index of refraction versus concentration. From the resulting calibration curve determine the concentration of the solution under test.

CHAPTER LV

Colorimetric and Spectrophotometric Analysis

280. General

Colorimetric and spectrophotometric methods of analysis are branches of photometric analysis based on the measurement of the absorption of light by a solution.

These methods are widely employed for the analysis of solutions and are based on the dependence of the absorption of light by a solution of a substance on the nature of the substance and its concentration in the solution. In both methods the concentration of the solute is determined by the degree of absorption of light passing through the test solution.

In colorimetry, absorption of wide bands of the visible spectrum or even the entire visible spectrum (white light) in coloured solutions is measured.

In spectrophotometry, absorption of monochromatic light is measured. This complicates the design of the instruments but offers the analyst great advantages over colorimetric methods. Spectrophotometric methods are used for the visible and ultraviolet regions of the spectrum.

In the simplest case the concentration of a substance is determined by the colour which develops when the substance dissolved in water or other suitable solvent forms intensely coloured ions or molecules. The intensity of the colour is compared with that of standard solutions of known concentration. This method is used, for example, in the analysis of organic dyes.

There are, however, only a few compounds of a colour sufficiently intense to be suitable for colorimetric determination. It is usually necessary to convert the colourless substance under test or its ions to a coloured compound and to determine the intensity of the colour of the resulting solution. The copper ion, for example, in aqueous solution is pale blue; but when ammonia is added, a complex is formed which is intense blue in colour. The ferric ion is converted into a yellow complex on the addition of sulphosalicylic acid in ammoniacal solution. Pale green solutions

of nickel salts change to bright red when dimethylglyoxime is added in the presence of an oxidant.

Coloured solutions are obtained by adding various reagents in a strictly definite order. Standard coloured solutions containing known quantities of the substance under test should be prepared in the same conditions.

281. Fundamental Laws

If a coloured solution is placed in a glass vessel with parallel walls (a cell) and a beam of light passed through it, some of the incident radiation is reflected from the cell walls, some is absorbed in the coloured solution, and some is transmitted (passes through the solution).

The intensity of the reflected light is negligible and constant when the same cell is used for a series of analyses, therefore, it may be disregarded and the following formula written:

$$I_0 = I_a + I_t$$

where I_0 = intensity of incident light (light entering a solution);
I_a = intensity of light absorbed by a solution;
I_t = intensity of transmitted light (light leaving a solution).

The relationship between these three magnitudes varies with the properties of a particular solution; it characterizes the optical properties of the solution, in other words, its ability to absorb and transmit light.

The absorption of light radiation as it passes through a coloured solution depends on two factors, namely the concentration of the solution and the distance (length) through which the light beam passes through it. This relationship, known as the combined Bouguer—Lambert—Beer law of light absorption, can be expressed as follows:

$$I_t = I_0 \cdot 10^{-\varepsilon l C}$$

whence

$$\log \frac{I_0}{I_t} = \varepsilon l C$$

where I_t = intensity of transmitted light;
I_0 = intensity of incident light;

l = length of the absorbing solution (or simply layer thickness), cm;
C = concentration of the solution, mole/lit;
ε = molar extinction coefficient.

The common logarithm of the ratio of the intensity of incident light to the intensity of transmitted light is known as the optical density, also called absorbance of the solution, and is expressed as

$$D = \log \frac{I_0}{I_t}$$

It follows therefore that the optical density of a solution is directly proportional to the concentration of the solution and the thickness of the absorbing layer.

282. Molar Extinction Coefficient

This is the coefficient of proportionality in the equation of the Bouguer—Lambert—Beer law and it is actually the optical density of a solution in which the concentration of the coloured substance is 1 mole per litre and the thickness of the absorbing layer is 1 cm. It depends on the properties of the solute, on its power to absorb light. The magnitude of ε varies for different substances within the range from several units to tens of thousands.

Only solutions that absorb light may be used in colorimetric and spectrophotometric analysis, and the accuracy and sensitivity of the determination is the greater, the more intensely light is absorbed.

The concentration and the layer thickness of a solution being constant, its optical density is determined by the molar extinction coefficient which is thus the measure of sensitivity of the colorimetric method.

283. Colour Intensity and Absorption Spectrum

As a beam of sunlight (white light) passes through a prism, it is dispersed into several coloured beams. Light rays of different colours are characterized by specific wavelengths which are measured in millimicrons (mμ), Angstroms (Å),

or in nanometres (nm)[1]. The visible region of the spectrum falls within the range of wavelengths from 400 to 760 mμ. Wavelengths from 100 to 400 mμ form the invisible ultraviolet region of the spectrum. Wavelengths over 760 mμ (up to 25 microns) make up the infra-red region of the spectrum.

The colour of solutions is characterized by their power to absorb certain wavelengths. Solutions absorbing in various regions of the visible spectrum appear to the observer as solutions of different colour. For example, a solution of potassium dichromate absorbs more intensely in the blue region and appears to the observer to be yellow. A solution of cuprammonium sulphate absorbs yellow radiation and as a result is coloured blue.

If a beam of white light falls on a cell, the apparent colour of the solution will be complementary to the colour absorbed in the solution.

Table 7 gives the wavelengths, the colour of the light absorbed in the solution, and the corresponding complementary colours which determine the apparent colour of the solution.

Table 7

Absorbed radiation		Colour as it appears to the observer
colour	wavelength, mμ	
Violet	400-450	Yellowish green
Blue	450-480	Yellow
Greenish blue	480-490	Orange
Bluish green	490-500	Red
Green	500-560	Purple
Yellowish green	560-575	Violet
Yellow	575-590	Blue
Orange	590-625	Greenish blue
Red	625-750	Bluish green

Dissolved substances having different chemical properties absorb different wavelengths. The optical density of

[1] In accordance with the SI International System, wavelengths are measured in nanometres; 1 millimicron = 1 nm = 10 Å.

a solution therefore depends on the wavelength of the incident light. The dependence of the optical density on the wavelength of incident light is an important factor characterizing the optical properties of solutions. This dependence is expressed graphically as an absorption curve obtained by plotting the wavelength of incident light as the abscissas and the optical density corresponding to these wavelengths as the ordinates.

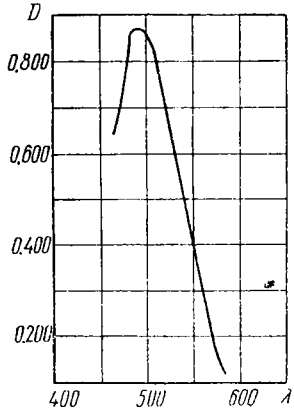


Fig. 49. Absorption curve of aqueous solution of Congo red dye
λ — wavelength of incident light in mμ; *D* — optical density

Sometimes the molar extinction coefficient ε is plotted on the axis of ordinates.

Figure 49 shows the absorption spectrum of an aqueous solution of Congo red. As seen from the curve, the solution absorbs most intensely at wavelengths of about 490 mμ. It is not necessary to have the graphical picture of the entire absorption spectrum to characterize a coloured solution. In many cases a coloured solution is fully characterized by the wavelength corresponding to its maximum absorption. This wavelength is denoted as λ_{max}. The value of the molar extinction coefficient for Congo red is maximum at an incident wavelength of 490 mμ. Spectrophotometers are used to obtain such a narrow band from the full spectrum of the visible light.

In many determinations it suffices to isolate a band of the spectrum from 20 to 100 mμ wide. This is accomplished with the aid of colour filters which by selective absorption of radiation allow a comparatively narrow band of wavelengths to pass. Glass colour filters are in common use; the colour of the filter corresponds to the region of the spectrum transmitted by it.

Many instruments intended for colorimetric determinations are complete with sets of colour filters which restrict the spectrum to the required narrow band and thus improve

the accuracy and sensitivity of the quantitative analysis.

If the region of maximum absorption or λ_{max} of the test solution is known, a colour filter having a maximum transmission close to λ_{max} should be used in the analysis.

Methods for selecting a suitable colour filter will be discussed in more detail in Sec. 293.

284. Measurement of Colour Intensity

The intensity of colour of a solution, or its optical density, is compared in colorimetry with the optical density of a solution of known concentration (standard solution), or with that of a solution that does not contain the unknown substance (reference solution). The colours are compared visually (by the standard series method described in Sec. 285 or by colour matching as described in Sec. 287), or with instruments employing a photoelectric cell (absorptiometers—see Sec. 291).

In visual colorimetry a colour match (equality of optical density) of the test and standard solutions is obtained by varying the thickness of the layer through which a light beam travels or by varying the concentration of the solution.

In accordance with the Bouguer—Lambert—Beer law, the optical density of the test solution is

$$D_x = \varepsilon l_x C_x \tag{1}$$

The optical density of the standard solution is

$$D_0 = \varepsilon l_0 C_0 \tag{2}$$

At the moment when the optical densities of the solutions become equal, i.e., $D_x = D_0$,

$$\frac{l_0}{l_x} = \frac{C_x}{C_0} \tag{3}$$

It follows therefore that when the optical densities are equal, the ratio of layer thickness in the two solutions is inversely proportional to the ratio of their concentrations. This relationship underlies the operating principle employed in the Duboscq colorimeter, where optical densities of two solutions are matched by varying the layer thickness of the test or the standard solution.

If the layer thickness in the solutions compared is equal, equality of their optical densities indicates equality of concentration of these solutions. The standard series method employs this relationship as the operating principle.

It follows, therefore, that quantitative colorimetric analysis consists essentially in measuring the optical density of a solution under specific conditions and determining the content of the unknown substance in the solution from the optical density.

Calibration curves are widely used in colorimetric and spectrophotometric analysis. A series of standard solutions containing known quantities of the substance under test is prepared beforehand, the optical density of each solution measured, and a calibration curve plotted, showing the relation between the optical density of a solution and its concentration. The optical density of each standard solution in the series is compared with that of the solvent or a reference solution which contains all the components of the test solution except the unknown substance. Light may be absorbed not only by the unknown substance, but by the solvent, as well as by other reagents that may be added to the solution. The purpose of the reference solution is to eliminate errors in analysis due to absorption of light by the solvent and reagents added to the solution.

The optical density of the test solution is measured in the same conditions as the optical density of the standard solutions and employing the same reference solution. The unknown substance is calculated from the calibration curve.

285. Standard Series Method

This is the simplest method of colorimetry, that requires no special apparatus. A series of standard solutions containing known quantities of the substance under test is prepared. The solutions are placed in test tubes or cylinders of the same size and shape and made from the same sort of glass. The test solution is poured into a similar test tube.

Graduated test tubes supplied with ground-in stoppers are very convenient for the purpose. Test tubes of 10-ml capacity are usually used.

They may be used for preparing the standard solutions by pouring into them predetermined volumes of the stock standard solution from a burette, adding the necessary reagents, and then diluting with water to the mark.

The test tubes are positioned in a rack in the order of increasing concentration and the colour of the test solution (in a similar test tube) is compared with the colours in the standard series.

The usual practice is to view the colour of the test and the standard solutions against the background of a sheet of white paper. The concentration of the substance in the test solution is the same as that in the standard solution whose colour matches the colour of the test solution.

The disadvantage of the standard series method is insufficient accuracy and the necessity of preparing a series of standards.

286. Determination of Copper in a Solution of Its Salt by the Standard Series Method

The pale blue colour of cupric sulphate solution is of an intensity insufficient for colorimetric determination.

On adding ammonia, the cuprous ions form intensely coloured complex ions of a blue colour:

$$Cu^{2+} + 4NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+}$$

In order to determine copper, first prepare a series of standard solutions containing known quantities of copper ions. Use recrystallized blue vitriol ($CuSO_4 \cdot 5H_2O$) as the starting material. First prepare a standard stock solution containing 0.5 or 1 g/lit of copper. Add a small quantity of sulphuric acid to the solution to inhibit hydrolysis of cupric sulphate in the solution. To obtain solutions with different copper contents, place accurately measured portions of the stock solution into special graduated test tubes, add ammonia (first to neutralize the sulphuric acid and then to form the complex copper ammoniate), and add water to the mark. Mix the solution.

In a similar way prepare the test solution: place an accurately measured portion of this solution into a measuring flask, add water to the mark, transfer a portion into a gra-

duated test tube, neutralize it, add the same amount of ammonia as in the standard series solutions, dilute with water to the mark, and mix.

Compare the intensity of colour with that of the standard series solutions against the background of a sheet of white paper. If the colour intensity of the test solution matches one in the standard series, this means that the copper content in both solutions is the same. If the colour intensity of the test solution falls between that of two neighbouring solutions in the standard series, the sought copper content will be the mean value of the copper content in the two standard solutions.

If the colour of the test solution is more intense than that of the most concentrated solution in the standard series, dilute the test solution and repeat the determination.

The copper content in the test solution is calculated from the known copper content in the standard solution (or adjacent solutions) in the series, whose colour matches that of the sample.

Example. Use cupric sulphate solution containing 1.0 g/lit of copper as the stock solution for preparing the standard series. Place from 0.5 to 5 ml of the stock solution (in 0.5 ml steps) into graduated 10-ml test tubes. Neutralize the solution with ammonia, add 3 ml of 2*N* ammonia solution to each tube, add water to the mark, and mix well.

The copper contents in the standard series solutions are:

Test tube	I	II	III	IV	V	VI	VII	VIII	IX	X
Stock solution, ml	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Copper content, g/lit	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50

Pipette 25 ml of the test solution into a 250-ml measuring flask and dilute with water to the mark. Transfer 5 ml of the resulting solution to a 10-ml graduated test tube and prepare a solution for the test in the same way as the standard solutions.

Suppose the colour intensity of the test solution matches that of the solution in test tube VIII. Hence, the copper content in the test solution is

$$\frac{0.4 \times 10 \times 250}{5 \times 25} = 8 \text{ g/lit}$$

287. Matching Colour Intensities by Varying the Viewing Depth

In this method the test and the standard coloured solutions are placed in two similar vessels. The layer thickness (depth) of one of the solutions is varied until the colours are matched. Since the concentration of the standard solution is known, that of the test solution can be calculated from formula (3) given in Sec. 284.

$$C_x = C_0 \frac{l_0}{l_x} \tag{3}$$

where C_x = concentration of the test solution;
C_0 = concentration of the standard solution;
l_x = layer thickness in the test solution;
l_0 = layer thickness in the standard solution.

It suffices to prepare only one standard solution in this method.

288. Visual Colorimeters of the Duboscq Type

Colorimeters of this type employ glass plungers that are immersed in flat-bottomed cups containing the test and the standard solutions. The viewing depth (the height or thickness of the liquid layer between the cup bottom and the lower end of the plunger) is varied by raising or lowering the plungers (or cups) until a colorimetric match is obtained.

In the simplest instrument of this type, the Duboscq colorimeter (see Fig. 50), a beam of light reflected from mirror *1* passes through two similar glass cups *2* positioned over the mirror. One cup contains the test and the other the standard solution. Two plungers *3* made of special optical glass are immersed in the solutions.

A rack-and-pinion mechanism raises or lowers the cups (or plungers) and thus the depth of the solutions varies.

In order to prevent overflow of the liquid displaced by the plungers when they are lowered (or the cups raised), the upper parts of the cups are wider in diameter. As a beam of light goes through the solution it passes through the plunger to fall on prism *4*, further passes through lens *5*, and enters eyepiece *6*. Absorption of the incident radiation in the cups depends on the thickness of the liquid layer and the concentration of the solution. The prisms bring the two beams into the eyepiece, whose field of vision is a circle divided into halves by a faint line. One half of the field is illuminated by the radiation passing through the test solution; the other half by the light passing through the standard solution. By varying the viewing depth in either solution (by raising or lowering the respective cup or plunger), the colours in the halves of the circular field are matched or, in other words, a photometrical equilibrium is attained. The rack-and-pinion mechanism has a vernier scale from which the viewing depth can be read to an accuracy of 0.1 mm.

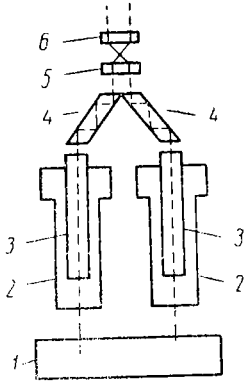


Fig. 50. Optical path in a colorimeter of the Duboscq type

1 — mirror; *2* — glass cups; *3* — plungers made of optical glass; *4* — prisms; *5* — lens; *6* — eyepiece

The concentration of the unknown solution is calculated from formula (3).

In an improved modification of the above-described colorimeter, the cups are stationary and only the plungers are moved. The colorimeter has a special illuminator and a set of colour filters that improve the accuracy of determinations because they make it possible to transmit light of a colour that is complementary to the colour of the solution under test.

In routine tests the optical densities of the solutions are not compared directly with a standard solution, but a series of standard solutions of known concentration are prepared beforehand, their optical densities are measured, and an optical density versus concentration calibration curve is plotted. The concentration of the test solution is then determined from the calibration curve.

289. Determination of Iron (III) with Duboscq-Type Colorimeter

This determination is based on the ability of trivalent iron to form coloured complexes with sulphosalicylic acid. The intensity of colour in solutions of this complex is proportional to the iron concentration. Depending on the pH of the medium, the ferric complexes have a different composition and their solutions differ in colour. The yellow trisulphosalicylic complex of iron formed in an alkaline medium at a pH from 8 to 11.5 is stable and it is suitable for analytical purposes. The required pH of the solution is adjusted by adding ammonium hydroxide.

The determination is carried out with a Duboscq-type colorimeter. The procedure is as follows. Prepare a standard solution containing a known quantity of chemically pure ferric-ammonium sulphate, place a portion of this solution in a measuring flask, add sulphosalicylic acid and aqueous ammonia solution, and mix the contents of the flask. Place a portion of the test solution into a similar measuring flask, add the same reagents in the same order, mix, and compare the colour intensities of the solutions. If these differ greatly, add an accurately measured portion of the standard or test solution to the respective flask (depending on which solution is more intensely coloured) and thus match the colour intensities in the solutions as close as possible. When the intensities of the colours in both solutions are almost the same, add water to the mark.

Place equal volumes of both solutions into the colorimeter cups, set the standard solution to a suitable layer thickness, and vary the viewing depth in the test solution until a colorimetric match is obtained.

The coloured complex of sulphosalicylic acid and iron in an alkaline medium absorbs at its maximum at a wavelength of 416 mμ. A blue filter should therefore be used when using a visual colorimeter provided with colour filters.

Example. Prepare a standard solution of ferric-ammonium sulphate containing 0.1 g/lit of iron. Place 25 ml of the test solution containing ferric iron into a 100-ml measuring flask and add water to the mark.

Place 10 ml of the standard solution into a 100-ml measuring flask, add 10 ml of 10 per cent sulphosalicylic acid and 10 ml of 10 per cent aqueous ammonia solution. Pour 10 ml of the diluted test solution into another 100-ml measuring flask and add the same reagents.

Suppose on mixing the contents in both flasks, the intensities of the colours developed in them are approximately equal. Add water to both flasks to the mark, mix, and pour the solutions into the cups of the colorimeter.

Suppose that the colorimetric match is attained at a height of the standard solution column $l_{st} = 7.00$ and that of the test solution $l_x = 5.20$.

Determine the iron content in the test solution from the following formula:

$$C_x = \frac{l_{st} \times 100 \times 0.1 \times 10 \times 100}{l_x \times 25 \times 100 \times 10} = \frac{7.00 \times 10}{5.20 \times 25} = 0.1538 \text{ g/lit}$$

290. Photometers

Another method for matching colour intensities in solutions consists in varying the intensities of the light beams passing through the solutions rather than the viewing depth. The instruments employing this principle are known as photometers.

In a well-known instrument of this type, namely the Pulfrich photometer, special diaphragms are inserted in the path of the light beam. The optical system of this instrument is very much like that of the Duboscq colorimeter, but instead of varying the viewing depth by means of plungers, the intensity of the beam of light is diminished by decreasing the aperture of the diaphragms on turning the drums connected to them.

The standard solution is placed into one cell and the reference solution into another. The reference solution contains all the reagents present in the standard solution except the unknown substance. As the reference solution is more transparent, one half of the field of vision will be brighter when the apertures of both diaphragms are fully opened. By manipulating the measuring drum, the diaphragm aperture is diminished until a photometric match is attained.

The measuring drums read the ratios of the diaphragm aperture area to the area of the fully opened diaphragm. Since the luminous flux passing through the diaphragm is proportional to the aperture area, the ratio of aperture areas is equal to the ratio of the luminous fluxes which determine the transmission of light by the standard solution (or its optical density).

The optical density of the standard solution is determined by reading the scale of the measuring drum at the moment when the photometric match is attained. A series of standard solutions is prepared, their optical densities measured, and an optical density versus concentration calibration curve plotted.

The optical density of the test solution is measured in the same way, and its concentration found from the calibration curve.

This method is very convenient for routine analyses carried out with a previously plotted calibration curve.

The above-described methods of comparing colour intensities in solutions are methods of visual colorimetry and are subject to personal error, i.e., the accuracy of determinations depends on the ability of the observer to distinguish small differences in intensity of colour. In routine analyses the eye becomes fatigued and is no longer able to do this. This disadvantage is eliminated in instruments in which the intensity of light beams is measured by a photocell.

291. Photoelectric Colorimeters (Absorptiometers)

In absorptiometers, or photoelectric colorimeters, intensities of light beams are measured in photocells.

A schematic diagram of an absorptiometer is shown in Fig. 51. A beam of light from incandescent lamp *6* is reflected from mirrors *5*, passes through colour filters *4* and cells *3*, and finally falls onto photoelectric cells *1*. The photocells and galvanometer *9* are connected on the opposition principle. If both cells produce equal currents (the intensity of the luminous fluxes is equal), they are balanced and the galvanometer reads zero. If, however, luminous

fluxes of different intensity fall onto the photocells, one being reduced due to absorption in a coloured solution, the galvanometer pointer deflects from zero.

Measuring diaphragm *7* controlled by measuring drum *8* and neutral optical wedges *2* are inserted into the paths of the light beams. By manipulating the measuring drum and changing the position of the smoky glass optical wedges, the intensities of the two beams can be matched.

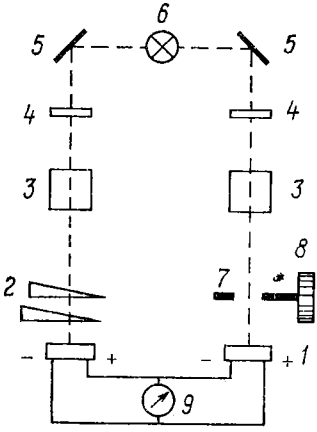


Fig. 51. Optical system of photoelectric colorimeter (absorptiometer)

1 — photocell; *2* — coarse and fine adjustment optical wedges; *3* — cell; *4* — colour filter; *5* — mirror; *6* — incandescent lamp; *7* — measuring diaphragm; *8* — measuring drum; *9* — galvanometer

Three similar cells are used with the absorptiometer. Two of them are intended to hold the reference solution while the third cell contains the coloured solution under test. By manipulating the measuring drum the diaphragm is set at the minimum aperture. The two cells containing the reference solution are inserted into the paths of both beams of light.

The solutions absorb equally, but since the intensity of light falling onto the right-hand photocell is diminished by the diaphragm, the galvanometer pointer deflects from zero. The currents produced in the photocells are balanced by introducing the optical wedges into the path of the left-hand light beam. This done, the galvanometer pointer reads zero again. If the right-hand cell containing the reference solution is replaced by a cell containing the coloured test solution, the intensity of the light passing through the latter will be diminished due to greater absorption of light and the current generated in the right-hand photocell reduced accordingly. The galvanometer pointer deflects from zero. By rotating the measuring drum the aperture in the diaphragm is enlarged and the luminous flux passing through it is intensified. At the moment when the intensities

of the two beams falling on the photocells are balanced, the galvanometer pointer reads zero and the measuring drum reads the optical density (or transmission) of the coloured test solution.

Practical determinations are carried out with a calibration curve which is previously plotted by measuring the optical densities of a series of standard solutions. The optical density of the test solution is measured in the same conditions and the concentration of the unknown substance determined from the calibration curve.

The cells, i.e., containers for the reference and test solutions, in colorimetric and spectrophotometric analysis are very important parts of the instrument. They are rectangular or cylindrical vessels having accurately measured distances between the walls, because it is not the total volume but the thickness of the solution through which a beam of light passes that actually matters.

The cells are manufactured of glass that transmits all wavelengths in the visible region of the spectrum. In ultraviolet spectroscopy, cells made of quartz and transmitting both the visible and the ultraviolet regions of the spectrum are used.

The surfaces upon which the beam of light falls and from which it emerges after it passes through the solution should be strictly parallel.

Measurement of optical density of solutions usually consists in matching the light transmitted through two similar cells, one containing the test and the other the reference solution. The selection of a cell having a greater or lesser layer thickness depends on the intensity of the solution colour. The greater the colour intensity of the solution, the smaller the layer thickness required. The error is minimum with optical densities from 0.3 to 0.5; therefore, cells ensuring optical densities within this range should be selected for the analysis.

Layer thickness in the reference cell should be the same as in the cell containing the test solution. Sets of cells supplied together with the instruments contain pairs of cells—one cell for the reference solution and the other for the test solution. Sets of cells for absorptiometers include two pairs for each thickness of liquid layer.

The working surfaces of the cells should be clean, since even small traces of dirt distort the results of the analysis. The cells therefore should first be washed with distilled water, then rinsed with the test solution, and only after that filled. The solutions should be filled into the cells immediately before the determination and should not be kept there longer than required for the analysis, since some substances may be easily adsorbed on the cell walls but

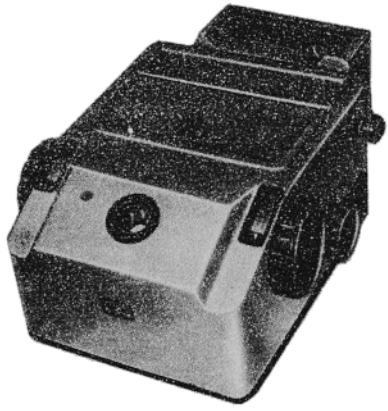


Fig. 52. Absorptiometer with electron tube indicator

removed from them with difficulty. After the determination has been completed, the cells should be emptied, washed, rinsed with distilled water, wiped with a piece of soft fabric on the outside, and inverted to allow water drops to drain from the inner surfaces. In no case should the cell walls be scraped, since that would deteriorate the optical properties of the cell. Only organic solvents or concentrated nitric acid may be used to remove contaminants from the cell surfaces if they cannot be eliminated as described above.

Soviet industry puts out several models of absorptiometers used in laboratory practice. The general arrangement of these instruments is similar and they only differ in the types of photocells used, systems for current amplification,

and number of colour filters supplemented. For example, one model is complete with nine narrow band filters which restrict the wavelengths to bands of 30-40 mμ. Another model includes only three colour filters, namely green, red, and blue. Each of them transmits a band of over 100 mμ and cannot be used to ensure a narrower band.

Fig. 52 shows the general view of an absorptiometer that, unlike the other instruments, employs an electron tube indicator as the null-instrument (instead of a galvanometer). When the currents generated in the two photocells are balanced, the sector on the lamp closes. The instrument is complete with ten colour filters and two sources of light, an incandescent lamp and a mercury-quartz lamp. Therefore, optical densities of solutions can be measured in both the visible and the near ultraviolet regions of the spectrum (at wavelengths of 313 and 367 mμ).

292. Determination of Nickel in an Aqueous Solution of Its Salt

The colorimetric determination of nickel ion is based on its ability to form a crimson complex with dimethylglyoxime and an oxidant in an alkaline medium. Bromine, iodine, or ammonium persulphate may be used as the oxidizing agent.

The coloured complex is unstable and even an excess of oxidant can decompose it. In order to ensure reproducible results it is necessary to observe the following order of mixing the components. First the oxidant, then dimethylglyoxime (alcoholic solution), and finally alkali should be added to the test solution containing the nickel salt. The solution should be diluted with water to a definite volume, mixed thoroughly, and its optical density measured with an absorptiometer.

This analysis should be done using a calibration curve. The procedure is as follows. First prepare a standard solution of chemically pure $NiSO_4 \cdot 7H_2O$. Acidify the solution slightly to prevent its hydrolysis. Transfer portions of the stock solution to measuring flasks, add equal quantities of the oxidant, dimethylglyoxime, and alkali and finally add water to the mark. Measure the optical densities of the

resulting solution and plot the optical density against concentration of nickel in the solution, i.e., a calibration curve.

Prepare the test sample in the same way and measure its optical density on the same instrument, using a solution containing all the reagents except nickel as the reference solution. Then determine the nickel content from the calibration curve.

293. Determination of Concentration of Organic Dyes

Calibration curves are usually used for determining the concentration of organic dyes. First a series of standard solutions is prepared containing known quantities of a reference dye. Depending on the properties of a particular dye, it is dissolved either in pure distilled water, or small amounts of acid or sodium carbonate are added. Some dyes that are insoluble in water (sulphur, vat dyes) are converted by special techniques into a form suitable for colorimetric analysis (for example, into a hydrosol, a stable suspension for which the relationship between the optical density and concentration of the solution holds true).

The optical densities of the prepared solutions are measured with an absorptiometer. The selection of a suitable colour filter markedly improves the sensitivity of the photometric determination.

When measuring the optical density, choose a colour filter that transmits the maximum light in the part of the spectrum in which the absorbance of the dye is maximum. If the maximum absorbance of the dye is not exactly known, choose a colour filter as follows: measure the optical density of the solution, inserting in succession all the colour filters; make the measurements against distilled water. The optical density of one and the same solution varies on measuring it with different colour filters. The filter that gives the maximum optical density is the most suitable for further work.

Using the colour filter chosen in this way, measure the optical densities of the standard solutions and prepare a calibration curve by plotting the concentrations of the reference dye (usually in grams per litre or milligrams per

litre) as abscissas and the corresponding optical densities as ordinates.

Dissolve an accurately weighed portion of the unknown dye in the same conditions as the reference dye. Then measure the optical density of the resulting solution in the same conditions as the standard solutions (in a similar cell and with the same colour filter). Find the concentration of the solution of the unknown dye from the calibration curve and then calculate the content of the dye in the weighed portion.

294. Spectrophotometers

In contrast to the instruments discussed above, spectrophotometers can be used to measure absorption of light radiation of different wavelengths (in different parts of the spectrum), or in other words, the optical density of a solution at a particular wavelength of the incident light.

The dependence of the optical density of a solution on the wavelength of incident light, expressed graphically and known as the absorption curve or simply absorption spectrum, is an important characteristic of the solute.

The main advantage of the spectrophotometer is that the optical density of a solution can be measured at the wavelength at which the solution absorbs at its maximum, i.e., at the maximum on the absorption curve, which is especially important in analysis of very dilute solutions.

Another advantage of the spectrophotometer is that two-component mixtures can be analyzed.

In a simple case, a region of the spectrum is selected on the absorption curve where practically only one solute absorbs, whereas the other component does not interfere with the determination.

There are two main types of spectrophotometers: one-cell and two-cell instruments. Fig. 53 shows the schematic diagram of a one-cell spectrophotometer. A beam of light from the source passes through a system of mirrors and falls onto quartz prism *2* that disperses the light beam into its component coloured rays which fall on mirror lens *1*. The latter focuses the reflected light on exit slit *3* of the instrument. By turning the prism, various regions of the

spectrum can be directed on the exit slit. As a result a practically monochromatic beam can be obtained, which passes quartz lens *4* and falls on the front wall of cell *5*, where part of the light is absorbed by the coloured solution in it. The light transmitted through the cell falls on photoelectric cell *6* to generate electric current which is amplified by an electron tube and balanced with the aid of a special opposition circuit incorporating a counting device.

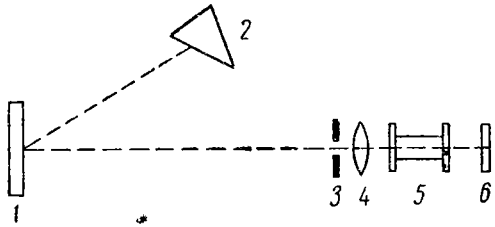


Fig. 53. Optical system of spectrophotometer
1 — mirror lens; *2* — quartz prism; *3* — exit slit; *4* — quartz lens; *5* — cell that holds the solution; 6 — photocell

The procedure is as follows. First the prism is set in the position corresponding to the desired wavelength. This is effected by manipulating a measuring drum calibrated in wavelengths. The cells are filled with the test and reference solutions, respectively, and installed in the instrument carriage. First the cell containing the reference solution is inserted into the path of the light beam and the current generated in the photocell is balanced by means of a special potentiometer to set the pointer of the galvanometer at zero. The carriage is now moved to install the test solution in place of the reference one. Since the optical density of the test solution is greater than that of the reference solution, the transmitted radiation is diminished accordingly, the current is reduced, and the galvanometer pointer is deflected from zero. By manipulating the control knob of the potentiometer the pointer is reset to zero and the optical density read off the scale on the potentiometer, which is calibrated in optical density units (from 0 to 2) and in per cent transmission (from 0 to 100).

The instrument is now set for measurement at another wavelength and the optical density of the solution is mea-

sured in this new region of the spectrum. The measurements thus obtained are tabulated and the absorption curve of the test solution is plotted from them.

Spectrophotometers can be used for measuring optical densities of solutions in the visible (400-760 mμ), ultraviolet regions (220-400 mμ) and the near infra-red (760-1100 mμ) regions of the spectrum. The instrument therefore has two sources of light, namely a hydrogen lamp

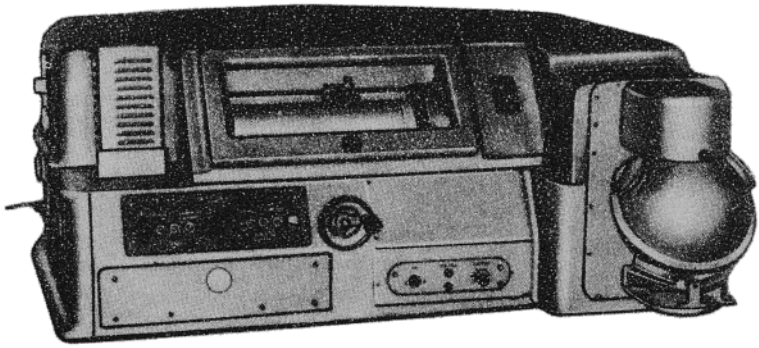


Fig. 54. Recording spectrophotometer

to measure in the region of wavelengths from 220 to 350 mμ and an incandescent lamp for wavelengths from 320 to 1100 mμ. Quartz cells are used for measuring in the ultraviolet region because common glass does not transmit ultraviolet radiation. The disadvantage of the spectrophotometer is that the optical density must be measured at each particular wavelength and then the absorption curve plotted.

Fig. 54 shows a spectrophotometer which automatically records absorption spectra in the visible region. In contrast to the one-cell spectrophotometer (see Fig. 53), this instrument employs two photocells, and equal beams of light pass simultaneously through two cells, one containing the reference and the other the test solution. The two beams are monochromatic radiation obtained by spectral dispersion of light generated by a cine-projector lamp.

The beams pass through the solutions in the two cells and are brought together onto a photocell. The photocurrent thus generated is amplified to move a carriage with a pen which records the absorption spectra on a chart paper fixed on a drum rotating synchronously with changes in wavelength of the incident monochromatic radiation.

The time required to obtain an absorption spectrum by this instrument is much less than by the one-cell spectrophotometer (an absorption spectrum in the visible region can be obtained in as little as 90 seconds). Its working range is however narrower (400-750 mμ instead of 220-1100 mμ).

295. Plotting Absorption Curves of Coloured Solutions

Plotting an absorption curve of a coloured solution involves measuring its optical density at different wavelengths and plotting the optical density (absorption) versus the wavelength of the incident light.

The absorption curve, often referred to as the absorption spectrum, is a very important characteristic of a chemical compound. The absorption spectra of dyes are of great practical significance because the colour of the dye and the dyed fabric depends on the ability of a particular dye to absorb certain wavelengths from the spectrum of sunlight. Technical specifications for organic dyes specify the absorption spectrum or the wavelength corresponding to the maximum absorption of a particular dye.

For example, Congo red absorbs at its maximum at 490 mμ; rhodamine G at 520 mμ; direct pure violet at 540 mμ; acid bright blue at 560 mμ; basic blue K at 600 mμ; basic turquoise at 620 mμ; and acid green G at 640 mμ.

The point of maximum absorption on the curve determines the colour of the dye and commercial dyes are checked for correspondence of the wavelength at maximum absorption to that of a standard sample. The check is effected by preparing in similar conditions a solution of the test dye and a standard dye, plotting their absorption curves, and comparing them. The wavelengths at maximum absorption should coincide to an accuracy of ±2-3 mμ. The concentra-

tion of the dye is checked simultaneously. Coincidence of the optical densities in the two solutions indicates equality of their concentrations.

296. Ultraviolet Spectrophotometry

Many substances which do not absorb in the visible region of the spectrum, and are therefore colourless, absorb ultraviolet rays intensely. Benzene, toluene, and acetone are examples of such substances.

Absorption curves for these substances can be obtained by ultraviolet spectrophotometric analysis. Like in the case of dyes, they also have an absorption maximum, but the latter lies in the ultraviolet region of the spectrum, i.e., beyond the visible region.

These substances are said to have "invisible colour" since the human eye cannot perceive the absorption of light in them. Aqueous solutions containing 1 and 10 per cent acetone, as well as alcoholic solutions containing various quantities of naphthalene, appear to the human eye (and therefore in visual colorimeters) to be of the same colour.

Absorption in the ultraviolet region obeys the same laws as in the visible region of the spectrum and the same spectrophotometer is employed for analysis.

Ordinary glass cells are not suitable in this case because glass is impervious to ultraviolet rays. Quartz cells are therefore used instead. It is very important to carefully wash the working surfaces of the cells, because even insignificant quantities of contaminants invisible to the eye will absorb in the ultraviolet region and distort the results of the analysis.

In addition to distilled water, organic solvents such as ethyl alcohol, cyclohexane, and chloroform are used as solvents in ultraviolet spectrophotometry.

The simplest kind of spectrophotometric analysis is the determination of an impurity that absorbs in a region of the ultraviolet spectrum in which the substance containing it does not absorb.

Benzene absorbs intensely in the region of wavelengths from 250 to 260 mμ. This property is employed for the quantitative determination of benzene admixtures in cyclo-

hexane, since the latter practically does not absorb in this region. The procedure is as follows. A standard solution containing 10 g of benzene in 1 litre of cyclohexane is prepared and its optical density measured at a wavelength $\lambda =$ $= 255$ mμ, using pure cyclohexane as the reference solution. Then in a cell of the same layer thickness (for example 1 cm) the optical density of the cyclohexane under test is measured at the same wavelength $\lambda = 255$ mμ. The content of benzene in the cyclohexane being rated is determined from the formula

$$C = 10 \times \frac{D_x}{D_{st}} \text{ g/lit}$$

where C = content of benzene in the cyclohexane under test;
D_x = optical density of the cyclohexane under test;
D_{st} = optical density of the standard solution.

Likewise, in the quantitative determination of divinylbenzene in styrene, the difference in their optical densities at a wavelength $\lambda = 313$ mμ is employed. The analysis is carried out by plotting a calibration curve.

Commercial captax (2-mercaptobenzothiazole rubber accelerator) contains various impurities which interfere with the determination of the basic substance by chemical analysis. These impurities do not absorb in the ultraviolet region where 2-mercaptobenzothiazole absorbs at its maximum. Commercial captax is analyzed by measuring the absorption of its alkaline solution (pH = 9.15) at a wavelength $\lambda = 309$ mμ and comparing the test results with the absorption of pure 2-mercaptobenzothiazole measured in the same conditions.

Example. Determination of 2-mercaptobenzothiazole in the commercial product.

(a) *Preparation of the standard solution.* Dissolve 0.2500 g of pure 2-mercaptobenzothiazole in 25 ml of 0.5*N* sodium hydroxide solution with heating to 50°C, cool, transfer quantitatively to a 500-ml measuring flask and dilute with water to the mark. Transfer 15 ml of this solution to another 500-ml flask and add an aqueous solution of borax (3.8 g/lit $Na_2B_4O_7 \cdot 10H_2O$) to the mark.

(b) *Measuring the optical density of the standard solution.* Fill the standard solution into a quartz cell having a layer

thickness of 4.098 mm and measure the optical density of the solution at a wavelength $\lambda = 309$ mμ.

Use an aqueous solution of borax as the reference solution. Suppose the results of measurements are as follows:

D_1	D_2	D_3	D_4	D_5	D_{mean}
0.698	0.700	0.700	0.702	0.700	0.700

(c) *Analysis of the commercial captax.* Dissolve 0.2500 g of captax weighed to the nearest 0.0002 g in NaOH solution as described for the preparation of the standard solution and add water to make up to 500 ml. Dilute 15 ml of this solution with the borax solution to make up to 500 ml.

Measure the optical density of the solution at $\lambda = 309$ mμ in a cell with a layer thickness of 4.098 mm. The borax solution should be used as the reference.

Suppose the results of measurements are as follows:

D'_1	D'_2	D'_3	D'_4	D'_5	D'_{mean}
0.676	0.678	0.676	0.680	0.678	0.678

Calculate the content of 2-mercaptobenzothiazole in commercial captax from the formula

$$x = \frac{D'_{mean}}{D_{mean}} \times 100\% = \frac{0.678}{0.700} \times 100\% = 98.80\%$$

CHAPTER LVI

Chromatographic Analysis

297. General

Chromatographic analysis is a method for separation of multi-component mixtures with subsequent determination of the individual components by chemical, physical, or physicochemical methods.

As a complex solution or mixture of gases (the moving phase) passes through a chromatographic column packed with finely-grained insoluble material (the stationary phase), the components are partly adsorbed on the solid or dissolved in the solvent it carries. The quantity of the adsorbed (or dissolved) component (gas or solute) depends on the nature of the adsorbing material (or solvent on it), the sorbed substance and the process conditions, namely, the temperature, pressure, and concentration. The process involved is called *sorption*; the absorbing material is called a *sorbent*; adhesion to the surface of a sorbent is called *adsorption.* The components can be selectively absorbed as molecules or ions and can form with the stationary phase sorption compounds of various stability. Under changed conditions (for example, at a different temperature or pressure), due to the action of solvents or other chemical reagents, the process can be reversed; *desorption* occurs, i. e., the components are transferred back to the solution or gaseous phase.

The chromatographic separation of a mixture is based on the difference in sorbability or solubility of its components. In other words, the processes of sorption and desorption of the various components proceed differently as they move through the sorbent.

As the test solution (or a gas mixture) passes through a chromatographic column (a tube filled with the sorbent) the components are taken up by the stationary phase and their content in the solution (gas) diminishes. As the solution (gas) continues to flow through the column, besides sorption, desorption occurs: the more strongly adsorbed (or more soluble) compounds lag behind the less strongly adsorbed (or less soluble) components. These processes occur over and over as the solution (or gas) moves downwards and the components form separate zones (bands) in the chromatographic column, i.e., are separated.

The separation is more effective if pure solvent (or neutral gas) is passed through the column after the test mixture has been charged.

The packing of the column is separated into several zones whose number (after complete separation) is equal to that of the components in the mixture.

There are several methods of chromatographic separation, but all of them are based on the distribution of the components between two immiscible phases, one of which is the stationary phase with a well-developed surface area, and the other is the moving phase, i.e., the gas or liquid stream flowing through the stationary phase.

The moving phase is the test mixture of liquids or gases; the stationary phase is a solid substance that reacts with the components of the mixture or a liquid solvent distributed on an inert solid support (carrier). In contrast to the solid adsorbent (or the liquid solvent) the carrier should be indifferent to the components of the test mixture. It only serves to support the liquid effecting separation.

There are several techniques for chromatographic separation of components:

Adsorption chromatography based on the difference in adsorption of various components on a solid.

Partition chromatography in which separation of the components is based on difference in solubility in two immiscible solvents one of which is a liquid film on the surface of the carrier. Separation of mixtures of gases or volatile substances by this method is of great practical importance. Blotting paper, usually filter paper, is often used as the carrier in partition chromatography. This modification of partition chromatography requiring no special apparatus is called paper chromatography.

Ion exchange chromatography based on exchange of ions between the components of the test mixture and the ionogenic groups of the ion exchanger material.

Precipitation chromatography based on the formation of precipitates as the analyzed mixture is passed through the column containing a mixture of the carrier and the precipitating agent. The latter is selected so that the precipitates formed by the components with the precipitating agent possess different solubility, which is responsible for the separation of the mixture into individual components.

The different types of chromatographic techniques are based on different processes which underlie them, *viz.*, adsorption, dissolution, and ion exchange. This makes it possible to select a suitable method for separation and analysis of various mixtures of inorganic and organic

compounds and makes chromatography applicable in research and industrial laboratories in all branches of the chemical and petrochemical industries.

Two chromatographic techniques will be discussed in detail, namely ion exchange chromatography, widely used for the analysis of electrolytes, and gas-liquid partition chromatography, the most important technique for separation and analysis of organic compounds.

298. Ion Exchange Chromatography

This method of separation is based on the exchange of ions between the test substance (in solution) and the sorbent (solid material).

The sorbents are ionogenic groups capable of dissociation and ion exchange with the solution to be analyzed. These materials are known as ion exchangers.

Two types of ion exchangers are distinguished, namely ionites exchanging their cations for those of the test solution and known as cation exchangers (cationites), and ionites capable of exchanging their anions for those of the test solution and referred to as anion exchangers (anionites).

Polymers containing ionogenic groups, for example sulpho groups or amino groups are widely used in the ion exchange processes. Inorganic ion exchange materials, such as alumina and silica gel are also used.

Prior to the analysis of the test mixture, the ion exchanger is washed free from low-molecular impurities, foreign ions (mainly iron ions), and converted into the requisite ionogenic form (essentially, insoluble acids, bases, or salts). Cation exchangers are converted to the H^+-form with hydrochloric acid, i.e., all the cations contained in the exchanger are replaced by hydrogen.

Anion exchangers are activated with alkali or soda to convert them to the OH^--form. Sometimes ion exchangers are converted to the salt-form, for example, the anion exchanger is converted to the chloride anionite and the cation exchanger to the Na^+-form.

As the test solution containing several cations passes through the cation exchanger, its cations are captured by the cationite, whereas an equivalent number of hydrogen

ions passes into the solution:

$$\text{cation exchanger-H} + Me^+ + X^- = \text{cation exchanger-Me} + H^+ + X^-$$

Depending on its properties (charge, volume, degree of hydration) the cation forms a more or less stable compound with the cation exchanger. If a suitable solvent is now passed through the column, the captured ions may be eluted from the exchanger and transferred back into the solution.

By selecting the appropriate conditions, even ions with closely similar properties can be separated.

The ion exchange process is widely used for separating the ions under test and for removing ions that interfere with the analysis. For example, the presence of iron interferes with the determination of molybdenum in steels. In chromatographic separation, molybdenum ions are taken up by the cation exchange resin from a strongly acidic solution.

On dissolving a steel sample in a mixture of hydrochloric and nitric acids, iron passes into solution and forms Fe^{3+} ions, whereas molybdenum is oxidized to the hexavalent state and forms MoO_2^{2+} ions. Ferric ions are not adsorbed from the strongly acidic solution and this difference in adsorbability of the two ions ensures their separation as the solution passes through a column packed with cation exchange resin. MoO_2^{2+} ions are adsorbed in the column. Complete separation is attained by subsequently passing 3-5 per cent alkali solution through the column. The MoO_2^{2+} ion is of a more acidic character than the Fe^{3+} ion and due to the action of the alkali, it passes into solution in the form of molybdate ion MoO_4^{2-}. The Fe^{3+} ion, even if it were absorbed by the cation exchanger, would not pass into the solution under the action of the alkali, because in these conditions it forms an insoluble hydroxide. For the quantitative determination of molybdenum, a strongly acidic solution containing molybdenum and iron ions is passed through a column packed with a cation exchange resin, then the column is washed with water, molybdenum is eluted with alkali, and its content determined by the permanganate method.

Iron ions are separated from zinc and aluminium ions by a similar procedure.

In analyzing a mixture of cations of the first three analytical groups, it is necessary to remove phosphate ion. This can be easily accomplished by passing the solution containing the mixture of cations and anions through a cation exchanger. Cations are taken up by the resin whereas anions, including the phosphate ion, remain in the solution. Then hydrochloric acid is passed through the cation exchanger; hydrogen ions displace the cations and the latter are eluted into a new solution free from phosphate ion.

The ion exchange method can be used for determining the salt content in a solution. As salt cations are adsorbed on the resin, an equivalent amount of hydrogen ions passes into the solution; the concentration of hydrogen ions is then determined by titration. For example, in the analysis of potassium chloride solution, it is passed through a cation exchanger, an equivalent amount of perchloric acid is produced, and the potassium chloride content of the test solution can be determined by titrating the perchloric acid with alkali. Salts of organic bases may be determined similarly; the cation is taken up by the ion exchange resin and an equivalent amount of the acid is produced.

The ion exchange process does not require complex apparatus. It may be used to separate and analyze mixtures of ions whose properties are very much alike, for example the ions of rare earth elements. The ion exchange process is also widely used for purifying water by removal of salts dissolved in it.

299. Gas-Liquid Partition Chromatography

A mixture of gases or vapours of volatile substances is passed through a column packed with a solid carrier soaked in a nonvolatile liquid (stationary phase). The carrier does not participate in the process but only serves to support the solvent. The main requirements for the carrier are inertness towards the components of the mixture to be separated and a well-developed area. Kieselguhr (diatom earth), Celite and a number of other materials are used as carriers.

In this method the effectiveness of separation does not depend on adsorption of the components but on their solubility in the liquid film which serves as the stationary phase. This liquid should dissolve all the components in the mixture under test, but dissolve them selectively. Moreover, it should be chemically inert, nonvolatile, and of low viscosity.

Depending on the properties of the components in a mixture, various liquids, such as mineral oil; triethylene glycol; benzyldiphenyl; dibutyl-, dioctyl-, and dinonyl-phthalates; tricresyl phosphate are used as the stationary phase. Silicone oil and other suitable lubricants are used for separation of substances with a high boiling point.

The amount of the stationary phase required depends on the nature of the components in the mixture and varies from 0.1 to 40 per cent of carrier weight.

An accurately measured sample is charged into the column where it is taken up by the stationary phase, mainly in its upper portion. Then a continuous stream of carrier gas (which does not react with the stationary phase nor with the components of the test mixture) is passed through the column. Nitrogen, carbon dioxide, hydrogen, helium, and sometimes air may be used as the carrier gas. As the gas passes through the column, the components of the mixture move along at different rates, depending on the properties of each component. Those components which are not readily soluble in the stationary phase are carried by the gas stream to a greater distance along the column. If the length of the column is sufficient, all the components of the mixture are isolated in separate zones. As the carrier gas continues to flow through the column, the separated components emerge from the exit of the column, one after another, the first being the component that is least soluble in the stationary phase. Each component is followed by discharge of a portion of pure carrier gas which separates the zones.

This method of analysis is called 'development' since the carrier gas 'develops' components, separating them into individual zones.

The effluent gas (emerging from the column) is delivered to a detector, whose sensitive element transforms some

physical characteristic of the gas to a signal which is transmitted onto a recording device.

Detectors whose operating principle is based on the measurement of thermal conductivity of the analyzed gases are most widely used for this purpose. They are not of very high sensitivity but are reliable in operation.

The action of thermochemical detectors is based on the changes in resistance of a platinum wire as it is heated with

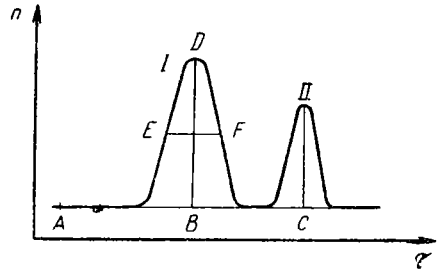


Fig. 55. Chromatographic curve
τ — time (or volume); n — stylus deviation.

burning gas emerging from the column. Although these instruments are very sensitive, their use is limited to cases where combustible gases are analyzed.

Very sensitive detectors are those which measure ionization currents arising as the gas passes through the detector chamber. The signal originating in the primary detector is transmitted to an automatic device which records it on a paper chart. An electron potentiometer is usually used to transform the detector signals to millivolt readings.

The detector, generally, is not an instrument that directly analyzes the effluent gas, since the signal emitted from the detector depends on the properties of the component and its concentration in the emerging gas stream. The detector can be used to detect the beginning and end of emergence of the component from the column.

Since the stream of gas passing through the column and the detector is incessant, the recorder draws a continuous line which is actually a chromatographic curve or simply a chromatogram (see Fig. 55).

As the pure carrier gas flows through the column (and the detector), the stylus draws a straight line (the base or zero line). At the moment *A*, a sample of gas under test is discharged into the column. Peak *I* (its middle point is *B*) corresponds to the emergence of the most volatile component of the mixture, i.e., the one which is retained to the least extent by the stationary phase. After the first component has passed, the properties of the gas emerging from the column approximate those of the carrier gas again and the effluent curve drops to the zero line. Peak *II* corresponds to the emergence of the second component in the mixture (its middle point is *C*). Thus, the effluent curve, or the chromatogram, has several peaks, their number being equal to that of the components contained in the mixture.

The distance from point *A* to the peak corresponds to the time during which the component passes through the column. The gas flow through the column being constant, a certain volume of the gas will correspond to this period of time. This time is known as the retention time; whereas the corresponding volume, as the retention volume.

The separation is more effective, the greater the difference in the retention volumes of the components in a mixture. As a rule, a component is characterized by the relative retention volume, that is the ratio of its retention volume to that of a standard.

The retention volume is determined by the rate of component passage through the column. Its magnitude determines the sequence in which the components emerge from the column. The smaller this magnitude, the earlier the component emerges. For example, in chromatographic separation of a mixture of hydrocarbon gases used in the manufacture of ethyl chloride (fraction C_2), with mineral oil as the stationary phase, the sequence of component emergence corresponds to successive increase in retention volume: methane, ethylene, ethane.

The chromatograph, the instrument used in gas-liquid partition chromatography consists of the following main units: a batching device used to introduce accurately measured amounts of the mixture to be analyzed; a chromatographic column where actual separation of the mixture takes

place; a detector (or the primary instrument) that accepts the emerging gas flow; a recording instrument; and auxiliary apparatus for maintaining the required pressure, temperature, and carrier-gas flow rate.

In routine determinations in industrial laboratories, the components of a mixture are usually known to the analyst and only their quantitative determination is required. This is accomplished, as a rule, with the aid of a calibration curve. First standard mixtures of the carrier gas with various quantities of the unknown component are prepared and passed through the chromatographic column; then the peak heights are measured and a calibration curve obtained by plotting the concentration of the component against the height of the peak. If determination of the concentration of several components is required, a calibration curve is plotted for each separate component. The test mixture is then passed through the column in the same conditions, the heights of the corresponding peaks measured, and the concentration of the unknown component determined from the calibration curve.

If the concentration of the component being determined is more or less constant, only one mixture containing the unknown component in a quantity equal to y (close to the expected one) is prepared. First the gaseous mixture to be analyzed is passed through the column and then, after some time has elapsed, the standard mixture is passed in the same conditions. The peaks, h_x and h_y, are measured and compared. The concentration of the unknown component x is determined from the formula

$$x = y \cdot \frac{h_x}{h_y}$$

The height of the peak is determined by the length of a perpendicular line drawn from the top of the peak to the zero line (*DB* in Fig. 55) and the content of the component in the mixture is calculated from this height. It can also be calculated from the area confined by the peak-forming curve and the base line. This area is usually found by multiplying the peak height by the peak half-width, that is the width measured at the middle of the height (*EF* in Fig. 55).

If the purpose of the analysis is to identify a particular compound, a portion of the supposedly present substance is added to the test mixture and if the supposition was correct, the height of the corresponding peak will grow. If the supposition was erroneous, a new peak will appear on the chromatographic curve. Sometimes it is necessary to repeat the analysis, employing different liquids as the stationary phase.

Gas-liquid partition chromatography is widely used in industry, especially for analyzing complex mixtures of components of similar properties, such as mixtures of hydrocarbons. This method is used to analyze, with sufficiently high accuracy, the hydrocarbons produced in processing oil. In the analysis of the butane fraction (fraction C_4) in oil cracking, it is possible to separate hydrocarbons whose boiling points differ quite insignificantly, e.g., isobutylene (b.p. 6.3°C) and butene-2 (b.p. 6.0°C). Gas-liquid partition chromatography is of great importance in the analysis of raw materials used in the production of polymers (ethylene, propylene, and their mixtures; divinyl; isoprene; etc.). This method is also used to separate mixtures of organic compounds, such as a mixture of mono-, di-, and trimethylamine in the presence of ammonia; a mixture of fatty (aliphatic) acids (from formic to dodecanoic); a mixture of the chlorine derivatives of methane; a mixture of phenylchlorosilanes.

By using various liquids in the stationary phase and by varying other conditions of the analysis (height of bed, column shape, flow rates, temperature, and others), a great variety of mixtures can be separated.

The methods of gas-liquid partition chromatography are constantly being improved. More effective separation can be achieved by heating the chromatographic column during separation of certain mixtures (chromatography at a preset temperature). The use of small glass capillary tubes as the carrier (capillary chromatography) also improves separation. Newly developed methods of separation and new highly sensitive detectors have made it possible to determine components present in a mixture in the minutest quantities, e.g., 0.00003 per cent acetylene in ethylene and 0.0000001 per cent hydrocarbons in air.

APPENDICES

Appendix 1

Atomic Mass of Some Elements

Element	Symbol	Atomic mass	Element	Symbol	Atomic mass
Aluminium	Al	26.9815	Magnesium	Mg	24.312
Antimony	Sb	121.75	Manganese	Mn	54.9380
Arsenic	As	74.9216	Mercury	Hg	200.59
Barium	Ba	137.34	Molybdenum	Mo	95.94
Bismuth	Bi	208.980	Nickel	Ni	58.71
Boron	B	10.811	Nitrogen	N	14.0067
Bromine	Br	79.909	Oxygen	O	15.9994
Cadmium	Cd	112.40	Phosphorus	P	30.9738
Calcium	Ca	40.08	Platinum	Pt	195.09
Carbon	C	12.00	Potassium	K	39.102
Chlorine	Cl	35.453	Radium	Ra	226.05
Chromium	Cr	51.996	Silicon	Si	28.086
Cobalt	Co	58.9332	Silver	Ag	107.870
Copper	Cu	63.54	Sodium	Na	22.9898
Fluorine	F	18.9984	Strontium	Sr	87.62
Gold	Au	196.967	Sulphur	S	32.064
Hydrogen	H	1.00797	Tin	Sn	118.69
Iodine	I	126.9044	Uranium	U	238.03
Iron	Fe	55.847	Zinc	Zn	65.37
Lead	Pb	207.19			

Appendix 2

Acid and Alkali Solutions Commonly Used in Analytical Chemistry

Reagent	Concentration of original solution	Concentration of prepared solution
Acid solutions		
Nitric acid, HNO_3		
concentrated	sp gr 1.42	69.8 per cent
6*N*	sp gr 1.42	385 ml per litre
2*N*	sp gr 1.42	128 ml per litre
Sulphuric acid, H_2SO_4		
concentrated	sp gr 1.84	95.6 per cent
2*N*	sp gr 1.84	55 ml per litre
Hydrochloric acid, HCl		
concentrated	sp gr 1.19	37.23 per cent
6*N*	sp gr 1.19	500 ml per litre
2*N*	sp gr 1.19	166 ml per litre
Acetic acid, CH_3COOH		
concentrated	sp gr 1.06	99.5 per cent
6*N*	80 per cent	420 ml per litre
2*N*	80 per cent	140 ml per litre
Tartaric acid, $H_2C_4H_4O_6$		150 g per litre
Alkali solutions		
Sodium hydroxide, NaOH		
6*N*		240 g per litre
2*N*		80 g per litre
Potassium hydroxide, KON		
6*N*		336 g per litre
2*N*		112 g per litre
Ammonia solution, NH_4OH		
concentrated	sp gr 0.91	25 per cent
6*N*	25 per cent	450 ml per litre
2*N*	25 per cent	150 ml per litre
Baryta water, $Ba(OH)_2$, saturated solution		72 g per litre
Lime water, $Ca(OH)_2$, saturated solution		17 g per litre

Appendix 3

REAGENTS

Chemical plants produce reagents of five grades of purity: (1) commercial, (2) purified, (3) pure, (4) analytical grade (A. R.), and (5) chemically pure (C. P.), indicating the highest grade of purity of a reagent (the least contaminated by impurities). Only reagents of A. R. or C. P. grade of purity may be used for analyses. Reagents of the other grades may be used for auxiliary purposes (for example, for obtaining hydrogen sulphide by the action of HCl on FeS; the preparation of chromium-sulphuric acid mixture for washing glassware).

A. Ion Test Solutions

(each solution contains 10 mg of ion per 1 ml)

Ion	Salt and its formula	g/lit*	Remarks**
Ag^+	Silver nitrate, $AgNO_3$	16	—
Hg_2^{2+}	Mercurous nitrate, $Hg_2(NO_3)_2 \cdot 2H_2O$	56	Dissolve in the presence of HNO_3
Pb^{2+}	Lead nitrate, $Pb(NO_3)_2$	83	—
Hg^{2+}	Mercuric nitrate, $Hg(NO_3)_2 \cdot 1/2H_2O$	82	Dissolve in the presence of HNO_3
Hg^{2+}	Mercuric chloride, $HgCl_2$	27	—
Bi^{3+}	Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$	80	Dissolve in 3*N* HNO_3
Cu^{2+}	Cupric nitrate, $Cu(NO_3)_2 \cdot 3H_2O$	60	—
Cd^{2+}	Cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$	150	—
Sb^{3+}	Antimonous chloride, $SbCl_3$	38	Dissolve in hydrochloric acid (1 : 1)
Sn^{2+}	Stannous chloride, $SnCl_2 \cdot 2H_2O$	56	Dissolve in the presence of HCl
Sn^{4+}	Stannic chloride, $SnCl_4 \cdot 5H_2O$	44	Dissolve in 3*N* HCl
Al^{3+}	Aluminium chloride, $AlCl_3 \cdot 6H_2O$	81	—
Al^{3+}	Aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$	139	—
Cr^{3+}	Chromic chloride, $CrCl_3 \cdot 6H_2O$	51	—
Cr^{3+}	Chromic nitrate, $Cr(NO_3)_3 \cdot 9H_2O$	77	—
Fe^{3+}	Ferric chloride, $FeCl_3 \cdot 6H_2O$	48	Dissolve in the presence of HCl
Fe^{3+}	Ferric nitrate, $Fe(NO_3)_3 \cdot 6H_2O$	62	—
Ni^{2+}	Nickelous nitrate, $Ni(NO_3)_2 \cdot 6H_2O$	145	—
Co^{2+}	Cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$	145	—
Mn^{2+}	Manganous nitrate, $Mn(NO_3)_2 \cdot 6H_2O$	142	—

Continued

Ion	Salt and its formula	g/lit*	Remarks**
Zn^{2+}	Zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$	149	—
Ba^{2+}	Barium chloride, $BaCl_2 \cdot 2H_2O$	122	—
Ba^{2+}	Barium nitrate, $Ba(NO_3)_2$	131	—
Sr^{2+}	Strontium nitrate, $Sr(NO_3)_2 \cdot 4H_2O$	106	—
Ca^{2+}	Calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$	118	—
Mg^{2+}	Magnesium nitrate, $Mg(NO_3)_2 \cdot 6H_2O$	128	—
K^+	Potassium nitrate, KNO_3	101	—
Na^+	Sodium nitrate, $NaNO_3$	85	—
NH_4^+	Ammonium nitrate, NH_4NO_3	80	—

* The number of grams specified for each salt should first be dissolved in a small volume of water and then the resulting solution is diluted to 1 litre with water.

** A dash in the Table indicates that the salt is soluble in water.

B. Special Reagents

Reagent	Preparation
Ammonium polysulphide (yellow), $(NH_4)_2S_2$	Add to 1 litre of ammonium sulphide solution 12 g of powdered sulphur, shake, allow to stand overnight, and separate the solution from the undissolved sulphur by filtration or decantation
Ammonium sulphate, $(NH_4)_2SO_4$	Dissolve 50 g of $(NH_4)_2SO_4$ in 100 ml of hot water, and after cooling, filter
Ammonium sulphide (colourless), $(NH_4)_2S$	Saturate 200 ml of concentrated ammonia solution with hydrogen sulphide until the gas is no longer absorbed; then add another 200 ml of concentrated ammonia solution and dilute to 1 litre with water
Ammonium mercurithiocyanate, $(NH_4)_2[Hg(SCN)_4]$	Dissolve 8 g of $HgCl_2$ and 9 g of NH_4SCN in 100 ml of water
Dimethylglyoxime (Chugaev's reagent), $CH_3 \cdot C(:NOH) \times$ $\times C(:NOH) \cdot CH_3$	Dissolve 1.2 g of dimethylglyoxime in 100 ml of 95 per cent alcohol

Continued

Reagent	Preparation
Diphenylamine, $(C_6H_5)_2NH$	Dissolve 0.5 g of diphenylamine in 100 ml of concentrated H_2SO_4
Iodine water, I_2	Dissolve 5 g of I_2 and 15 g of KI in as little water as possible and, after the iodine has dissolved, dilute to 1 litre with water
Potassium dihydrogen antimonate, KH_2SbO_4	Dissolve 22 g of KH_2SbO_4 in 1 litre of hot water and boil for 2 minutes. After cooling, add 35 ml of 6*N* KOH solution; allow to stand overnight and filter
Starch	Wet 2.5 g of soluble starch with 5 ml of water and pour the resulting mass into 100 ml of boiling water, boil for 1-2 minutes, and after cooling, add 5 drops of toluene
Magnesia mixture, $MgCl_2 + NH_4Cl + NH_4OH$	Dissolve 160 g of ammonium chloride and 180 g of magnesium chloride in water, add 150 ml of concentrated ammonia solution, and dilute to 1 litre with water
Molybdenum solution	Dissolve 150 g of ammonium molybdate in 1 litre of water. Slowly add the resulting solution, stirring constantly, to a mixture of 500 ml of concentrated HNO_3 (sp gr 1.4) and 500 ml of water in which 300 g of ammonium nitrate have previously been dissolved
Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$	Dissolve 23 g of sodium nitrite in 50 ml of water, add 10 g of cobalt nitrate and then 20 ml of 5*N* acetic acid. Dilute the resulting solution to 100 ml with water, allow to stand overnight, and filter or decant. The reagent decomposes on standing for a long time
Sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$	Dissolve 3 g of sodium nitroprusside in 100 ml of water
Sodium sulphide + sodium hydroxide, $Na_2S + NaOH$	Dissolve 480 g of $Na_2S \cdot 9H_2O$ and 40 g of NaOH in 1 litre of water

Continued

Reagent	Preparation
Nessler's reagent	Dissolve 50 g of KI in 50 ml of water; to the resulting solution add gradually a saturated solution of $HgCl_2$ (6 g per 100 ml of water) until a stable precipitate of HgI_2 appears; then add 200 ml of 6*N* NaOH and dilute to 500 ml with water; keep in a dark place
Hydrogen peroxide (3 per cent solution), H_2O_2	Dilute 10 ml of 30 per cent H_2O_2 to 100 ml with water
Griess' reagent — a mixture of sulphanilic acid and α-naphthylamine solutions	Prepare two solutions: (1) dissolve 0.5 g of sulphanilic acid in 150 ml of 2*N* acetic acid; (2) dissolve 0.22 g of α-naphthylamine in 200 ml of water, with heating. To the colourless solution add 150 ml of 2*N* acetic acid. Mix the two solutions and keep in a dark place
Hydrogen-sulphide water	Saturate an aqueous hydrogen-sulphide solution with hydrogen sulphide gas
Fuchsine (magenta)	Dissolve 0.1 g of fuchsine in 100 ml of water
Fuchsine, decolourized (Schiff's reagent)	Pass a stream of SO_2 through a fuchsine solution prepared as described above
Chlorine water, Cl_2	Prepare (in the cold) a saturated aqueous solution of chlorine
Zinc uranyl acetate, $Zn(UO_2)_3(CH_3COO)_8$	To 55 ml of water add 10 g of uranyl acetate, 30 g of zinc acetate, and 9 ml of 6*N* acetic acid. Heat until the components are dissolved, add water to make up to 100 ml, allow to stand for 24 hours, and filter
Alizarin-S reagent	Dissolve 0.25 g of Alizarin-S in 100 ml of water
Formiate buffer solution	Dissolve 2.8 g of sodium formiate in 100 ml of 98 per cent formic acid
8-Hydroxyquinoline, C_9H_6NOH	Dissolve 5 g of 8-hydroxyquinoline in 95 ml of water

Appendix 4

Density of Solutions of Strong Acids, Alkalies, and Ammonia at 20°C, g/cm³

Concentration, per cent	H_2SO_4	HNO_3	HCl	KOH (15°C)	NaOH	NH_3
2	1.012	1.009	1.008	1.016	1.021	0.990
4	1.025	1.020	1.018	1.033	1.043	0.981
6	1.038	1.031	1.028	1.048	1.065	0.973
8	1.052	1.043	1.038	1.065	1.087	0.965
10	1.066	1.054	1.047	1.082	1.109	0.958
12	1.080	1.066	1.057	1.100	1.131	4.950
14	1.095	1.078	1.068	1.118	1.153	0.943
16	1.109	1.090	1.078	1.137	1.175	0.936
18	1.124	1.103	1.088	1.156	1.197	0.930
20	1.139	1.115	1.098	1.176	1.219	0.923
22	1.155	1.128	1.108	1.196	1.241	0.916
24	1.170	1.140	1.119	1.217	1.263	0.910
26	1.186	1.153	1.129	1.240	1.285	0.904
28	1.202	1.167	1.139	1.263	1.306	0.898
30	1.219	1.180	1.149	1.286	1.328	0.892
32	1.235	1.193	1.159	1.310	1.349	—
34	1.252	1.207	1.169	1.334	1.370	—
36	1.268	1.221	1.179	1.358	1.390	—
38	1.284	1.234	1.189	1.384	1.410	—
40	1.303	1.246	1.198	1.411	1.430	—
42	1.321	1.259	—	1.437	1.449	—
44	1.338	1.272	—	1.460	1.469	—
46	1.357	1.285	—	1.485	1.487	—
48	1.376	1.298	—	1.511	1.507	—
50	1.395	1.310	—	1.538	1.525	—
52	1.415	1.322	—	1.564	—	—
54	1.435	1.334	—	1.590	—	—
56	1.456	1.345	—	1.616	—	—
58	1.477	1.356	—	—	—	—
60	1.498	1.367	—	—	—	—
62	1.520	1.377	—	—	—	—
64	1.542	1.387	—	—	—	—
66	1.565	1.396	—	—	—	—
68	1.587	1.405	—	—	—	—
70	1.611	1.413	—	—	—	—
72	1.634	1.422	—	—	—	—
74	1.657	1.430	—	—	—	—
76	1.681	1.438	—	—	—	—
78	1.704	1.445	—	—	—	—
80	1.727	1.452	—	—	—	—
82	1.749	1.459	—	—	—	—

Continued

Concentration, per cent	H_2SO_4	HNO_3	HCl	KOH (15°C)	NaOH	NH_3
84	1.769	1.466	—	—	—	—
86	1.787	1.472	—	—	—	—
88	1.802	1.477	—	—	—	—
90	1.814	1.483	—	—	—	—
92	1.824	1.487	—	—	—	—
94	1.8312	1.491	—	—	—	—
96	1.8355	1.495	—	—	—	—
98	1.8365	1.501	—	—	—	—
100	1.8305	1.513	—	—	—	—

Appendix 5

Dissociation Constants of Weak Electrolytes

Electrolyte	Dissociation constant at 25°C	$pK = -\log K$
Ammonia solution, NH_4OH	$1.8 \cdot 10^{-5}$	4.74
Nitric acid, HNO_2	$5.1 \cdot 10^{-4}$	3.29
Sulphurous acid, H_2SO_3	$K_1 = 1.3 \cdot 10^{-2}$	$pK_1 = 1.89$
	$K_2 = 6.3 \cdot 10^{-8}$	$pK_2 = 7.20$
Hydrogen sulphide, H_2S	$K_1 = 8.9 \cdot 10^{-8}$	$pK_1 = 7.05$
	$K_2 = 1.3 \cdot 10^{-13}$	$pK_2 = 12.90$
Hydrocyanic acid, HCN	$6.2 \cdot 10^{-10}$	9.21
Carbonic acid, H_2CO_3	$K_1 = 4.5 \cdot 10^{-7}$	$pK_1 = 6.35$
	$K_2 = 4.8 \cdot 10^{-11}$	$pK_2 = 10.32$
Phosphoric acid, H_3PO_4	$K_1 = 7.6 \cdot 10^{-3}$	$pK_1 = 2.12$
	$K_2 = 6.2 \cdot 10^{-8}$	$pK_2 = 7.21$
	$K_3 = 4.4 \cdot 10^{-13}$	$pK_3 = 12.36$
Tartaric acid, $H_2C_4H_4O_6$	$K_1 = 9.1 \cdot 10^{-4}$	$pK_1 = 3.04$
	$K_2 = 4.3 \cdot 10^{-5}$	$pK_2 = 4.37$
Formic acid, HCOOH	$1.8 \cdot 10^{-4}$	3.75
Acetic acid, CH_3COOH	$1.74 \cdot 10^{-5}$	4.76
Oxalic acid, $H_2C_2O_4$	$K_1 = 5.6 \cdot 10^{-2}$	$pK_1 = 1.25$
	$K_2 = 5.4 \cdot 10^{-5}$	$pK_2 = 4.27$

Appendix 6

Solubility Products (S) of Sparingly Soluble Substances at Room Temperature

Substance	Molecular weight	S	pS
AgCl	143.34	$1.78 \cdot 10^{-10}$	9.75
AgBr	187.80	$5.3 \cdot 10^{-13}$	12.28
AgI	234.79	$8.3 \cdot 10^{-17}$	16.08
Ag_2CrO_4	331.77	$1.1 \cdot 10^{-12}$	11.95
$BaCO_3$	197.37	$5.1 \cdot 10^{-9}$	8.29
BaC_2O_4	225.38	$1.7 \cdot 10^{-7}$	6.77
$BaCrO_4$	253.37	$1.2 \cdot 10^{-10}$	9.92
$BaSO_4$	233.43	$1.1 \cdot 10^{-10}$	9.96
$CaCO_3$	100.09	$4.8 \cdot 10^{-9}$	8.32
CaC_2O_4	128.10	$2.3 \cdot 10^{-9}$	8.64
$CaSO_4$	136.15	$2.5 \cdot 10^{-5}$	4.60
CuS	95.61	$6.3 \cdot 10^{-36}$	35.20
CdS	144.48	$7.9 \cdot 10^{-27}$	26.10
FeS	87.92	$3.2 \cdot 10^{-18}$	17.50
Fe_2S_3	207.90	$1 \cdot 10^{-88}$	88.00
$Fe(OH)_2$	89.87	$1 \cdot 10^{-15}$	15.00
$Fe(OH)_3$	106.87	$3.2 \cdot 10^{-38}$	37.50
HgS	232.68	$4 \cdot 10^{-53}$	52.40
$MgCO_3$	84.33	$4 \cdot 10^{-5}$	4.40
$Mg(OH)_2$	58.33	$6 \cdot 10^{-10}$	9.22
$MgNH_4PO_4$	137.34	$2.5 \cdot 10^{-13}$	12.60
MnS	87.01	$2.5 \cdot 10^{-10}$	9.60
NiS	90.78	$1.0 \cdot 10^{-24}$	24.00
PbS	239.28	$2.5 \cdot 10^{-27}$	26.60
$PbSO_4$	303.28	$1.6 \cdot 10^{-8}$	7.80
$PbCrO_4$	323.22	$1.8 \cdot 10^{-14}$	13.75
$PbCl_2$	273.12	$1.6 \cdot 10^{-5}$	4.79
PbI_2	461.03	$1.1 \cdot 10^{-9}$	8.98
$Pb_3(PO_4)_2$	811.58	$7.9 \cdot 10^{-43}$	42.10
$SrCO_3$	147.64	$1.1 \cdot 10^{-10}$	9.96
SrC_2O_4	175.65	$5.6 \cdot 10^{-8}$	7.25
$SrSO_4$	183.70	$3.2 \cdot 10^{-7}$	6.49
$Zn(OH)_2$	99.40	$7.1 \cdot 10^{-18}$	17.15
ZnS	97.45	$1.6 \cdot 10^{-24}$	23.80

Appendix 7

Standard Oxidation-Reduction Potentials of Oxidizing and Reducing Agents

Initial state	Final state	Electronic-ionic equation	Oxidation-reduction potential, V
Cl_2	$2Cl^-$	$Cl_2 + 2e = 2Cl^-$	+1.36
Br_2	$2Br^-$	$Br_2 + 2e = 2Br^-$	+1.09
I_2	$2I^-$	$I_2 + 2e = 2I^-$	+0.54
NO_3^-	NO_2	$NO_3^- + 2H^+ + 1e = NO_2 + H_2O$	+0.80
NO_3^-	NO	$NO_3^- + 4H^+ + 3e = NO + 2H_2O$	+0.96
H_2O_2	H_2O	$H_2O_2 + 2H^+ + 2e = 2H_2O$	+1.77
MnO_4^-	MnO_4^{2-}	$MnO_4^- + 1e = MnO_4^{2-}$	+0.56
MnO_4^- (in acidic solution)	Mn^{2+}	$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	+1.51
MnO_4^- (in neutral or alkaline solution)	MnO_2	$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$	+0.60
$Cr_2O_7^{2-}$ (in acidic solution)	$2Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	+1.33
CrO_4^{2-} (in alkaline solution)	CrO_2^-	$CrO_4^{2-} + 2H_2O + 3e = CrO_2^- + 4OH$	−0.13
$S_2O_8^{2-}$	$2SO_4^{2-}$	$S_2O_8^{2-} + 2e = 2SO_4^{2-}$	+2.0
SO_4^{2-}	SO_3^{2-}	$SO_4^{2-} + 2H^+ + 2e = SO_3^{2-} + H_2O$	+0.17
S	H_2S	$S + 2H^+ + 2e = H_2S$	+0.14
$S_4O_6^{2-}$	$2S_2O_3^{2-}$	$S_4O_6^{2-} + 2e + 2S_2O_3^{2-}$	+0.09
$S_2O_3^{2-}$	2S	$S_2O_3^{2-} + 6H^+ + 4e = 2S + 3H_2O$	+0.5
AsO_4^{3-}	AsO_3^{3-}	$AsO_4^{3-} + 2H^+ + 2e = AsO_3^{3-} + H_2O$	+0.56
PbO_2	Pb^{2+}	$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	+1.46
Fe^{3+}	Fe^{2+}	$Fe^{3+} + 1e = Fe^{2+}$	+0.77
Sn^{4+}	Sn^{2+}	$Sn^{4+} + 2e = Sn^{2+}$	+0.15

Logarithms

No.	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13

30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Continued

No.	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5

76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	4
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	4
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	[illegible]	9996	0	1	1	2	2	3	3	3	4

Antilogarithms

log	0	1	2	3	4	5	6	7	8	9	Proportional parts							
											2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3

22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	0	1	2	2	3	3	4	4	5
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Continued

Log	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	5	6	7
54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11

73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7596	2	3	5	7	8	10	12	13	15
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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